

HAZARD ASSESSMENT OF MANAGEMENT OF WASTE LITHIUM BATTERIES

by

B.G. Vincent  
Factory Mutual Research Corporation  
Norwood, Massachusetts 02062

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Project Officer

Florence Richardson  
Office of Solid Waste  
Environmental Protection Agency  
401 M Street SW  
Washington, D.C. 20460

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## ABSTRACT

The purpose of this study was to assess the hazards associated with the disposal of waste lithium batteries using existing lithium battery safety test and accident data. First, a survey was conducted to determine 1) basic cell constituents and electrochemical reaction by-products of the various lithium batteries, and 2) products of reactions between cell constituents and water or heat. Next, a survey of solid waste disposal techniques was conducted. This involved the identification of both waste lithium battery management practices and conventional solid waste disposal techniques. Using the information from this survey, the hazards associated with the collection, processing, and disposal of waste lithium batteries were assessed.

A survey of lithium battery safety test and accident data indicated that abuse test procedures for lithium cells frequently simulated hazardous conditions anticipated in disposal operations. Abuse test data were then used in evaluating the behavior of lithium batteries during disposal operations. However, published results of abuse tests and toxicity data were incomplete for several generic electrochemical systems, and did not take into account manufacturer variations in cell construction and safety features. For this reason, it is recommended that standardized abuse tests be used for testing lithium batteries to determine their hazard potential. In the interim, until such data can be generated and reviewed, the following conclusions were made.

1) Lithium-thionyl chloride and lithium-sulfur dioxide batteries should be considered potential safety hazards if processed using conventional waste disposal methods.

2) Several lithium battery systems, (lithium-sulfur dioxide, lithium-thionyl chloride, lithium-manganese dioxide and lithium vanadium pentoxide) contain highly toxic compounds which may contaminate the environment if released. These systems should be considered potentially dangerous to the environment.

3) Because of safety and environmental considerations, lithium batteries, as a class, should not be incinerated.

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## SECTION 1

### INTRODUCTION

Like most battery systems, lithium primary<sup>†</sup> cells are constructed using a variety of materials which are either toxic, reactive, corrosive, or combustible.

Since their introduction in 1970<sup>(1,2)</sup>, attention has been drawn to lithium batteries as the result of several accidents which have occurred during the use or test of these cells. In view of this, much of the lithium battery research in recent years has been directed toward improving lithium battery operational safety. The result has been chemistry modifications and the development of low pressure vents, fuses, and diodes which significantly reduce the operational hazards. However, the basic electrochemical components of these cells remain the same and therefore the accident potential of these systems must still be recognized. As these cells find increasing use in military, industrial, and consumer applications, it becomes necessary to determine whether the hazards associated with their disposal warrant their classification and control as "hazardous wastes." This is the basic objective of this study.

To accomplish this objective, it was necessary to 1) identify potentially hazardous lithium cell components and their properties, 2) characterize conventional waste disposal hazards as they relate to lithium batteries, and 3) develop a methodology for interpreting existing lithium battery safety test data to evaluate the anticipated disposal hazards. The scope of work required that the program objective be executed without the conduct of tests.

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<sup>†</sup>Nonrechargeable cells

## SECTION 2

### SUMMARY

The objective of this study was to assess the hazards associated with the disposal of waste lithium batteries and to make the determination as to whether or not they should be classified as "hazardous wastes" for disposal purposes.

To accomplish the cited program objective, it was first of all necessary to identify the hazards of the various chemicals in lithium primary battery systems. This entailed not only the identification of basic cell constituents but also the identification of those compounds occurring as by-products of electrochemical reactions taking place within a given cell during discharge. Further, to assist in the quantification of safety and environmental hazards, it was also necessary to determine the products of reactions between cell constituents and water or heat for those situations where the structural integrity of the cell is compromised. Once cell materials and reaction by-products were identified, safety and toxicity classification<sup>(3-8)</sup> data were consulted to assess safety and environmental hazards.

The data indicated that the lithium-thionyl chloride, lithium-sulfur dioxide, lithium-manganese dioxide, lithium-iodine, and lithium-vanadium pentoxide systems contain at least one highly toxic chemical or compound as a basic cell component. Five systems, lithium-thionyl chloride, lithium-sulfur dioxide, lithium-polycarbon monofluoride, lithium-iron sulfide, and lithium-vanadium pentoxide contain elements which will produce hazardous by-products when contacted by water. All nine lithium battery systems surveyed during this study have components which will generate hazardous gases when heated to decomposition.

Next, a survey of solid waste disposal techniques was conducted. This survey was executed in two phases.

First, a survey of lithium battery disposal techniques used by battery manufacturers and specialty organizations was made. The survey included a review of processing techniques, battery neutralization and disposal methods, and accident experience. Most of this information came from personal communication with battery industry manufacturers or their representatives since very little information existed in the literature.

The second phase was an assessment of conventional municipal and industrial waste disposal techniques, specifically geared toward determining the equipment

and processes used for handling solid waste and rubbish. Using the information from this survey, the hazards associated with the collection, processing, and disposal of waste lithium batteries via conventional waste disposal operations were determined.

Hazardous situations created by conventional waste processing operations are: 1) mechanical shock - caused by throwing, dropping, or rough handling during collections or explosion in a processing unit (baler, compactor or shredder) during processing; 2) external short circuit - the result of bridging battery terminals by electrically conductive materials contained in the trash; 3) immersion in water or moist material; 4) crushing - caused by shredding or compacting operations (during collection or processing) or grading equipment at the disposal site; 5) elevated temperature/fire - caused by spontaneous heating of organic matter in the trash or an incineration operation; and 6) foreign object penetration - rupture or puncture by adjacent material during compacting or landfilling operations. The hazardous situations may result in lithium battery explosion, fire, internal exothermic reactions, or hazardous material releases.

Once potential hazards were defined, efforts were made to assess the effects of these hazards during disposal operations. These hazard assessments were based upon published physical abuse test (incineration, mechanical shock, crushing, etc.) data for various lithium cells. The test procedures frequently simulated hazardous situations anticipated in disposal operations. By correlating abuse test data to potential accident scenarios, a reasonable assessment of the behavior of lithium batteries in conventional waste disposal operations was made.

The review of abuse test data revealed the following:

1) External short circuit tests of unfused lithium-sulfur dioxide, lithium-thionyl chloride and lithium-polycarbon monofluoride cells resulted in the activation of vent mechanisms. Certain lithium-thionyl chloride cells also deformed and exploded under external short circuit conditions.

2) Immersion (in fresh or salt water) and drop tests of intact cells at approximately 25°C produced no hazardous situation.

3) Cell deformation (crush) tests resulted in the venting of lithium-sulfur dioxide cells.

4) Foreign object penetration tests caused minor heating (10°-20°C) in lithium-copper oxide cells and explosion in lithium-thionyl chloride cells.

5) Explosions are likely if the internals of lithium cells are allowed to reach the melting point of lithium (approximately 180°C).

Conclusions based upon this hazard evaluation are presented in Section 3 of this report.



### SECTION 3

#### CONCLUSIONS AND RECOMMENDATIONS

Lithium battery disposal hazards can be divided into two broad categories: 1) immediate hazards for disposal workers handling the batteries, and 2) long-range hazards to the environment and the neighboring populace.

Hazards to disposal workers can best be determined from standardized abuse tests similar to those described in Appendix A. Some published abuse test data results are available, but further testing is needed to provide a comprehensive, updated data base covering all lithium cell designs, i.e., including important variations among manufacturers. In lieu of a standardized abuse test data base, the following interim generic hazard classifications are offered based on battery component toxicity/flammability/reactivity data, accident reports, and the correlation of available abuse test data to abuses incurred during disposal.

1) Lithium-thionyl chloride and lithium-sulfur dioxide batteries should be temporarily classified as hazardous because they can explode, burn, and/or vent toxic fumes during conventional municipal solid waste disposal operations. If and when manufacturers of these batteries submit documented evidence that their particular cells should be rated low hazard or nonhazardous when subjected to the types of abuse tests in Appendix A, their cells should be exempted from this hazardous classification.

2) The remaining lithium battery systems surveyed (lithium-carbon monofluoride, lithium-manganese dioxide, lithium-iodine, lithium-iron sulfide, lithium-copper oxide, lithium-silver chromate and lithium vanadium pentoxide) should not be classified as hazardous to disposal workers because they do not present the same safety hazard as do the thionyl chloride and sulfur dioxide systems. During this study no cases of fire or explosions initiated by these systems were documented. With possible exception of incineration, the abuse test data reviewed gave virtually no indication of safety problems with these systems.

3) All lithium battery systems are hazardous to nearby personnel and the environment when they are incinerated; therefore, incineration should be prohibited.

With regard to the long-range hazard to the environment and surrounding populace it was determined that six of the lithium battery systems surveyed in this study (lithium-sulfur dioxide, lithium-thionyl chloride, lithium-manganese dioxide, lithium-iodine, lithium-polycarbon monofluoride and lithium-vanadium pentoxide) may contain highly toxic compounds which will contaminate the environment if released. The actual environmental impact will be a function of the concentration of cells disposed in a given location, as well as the (currently unspecified) quantities of these toxic materials in individual cells. The decision as to whether to classify these batteries as environmentally hazardous should be delayed until data on material quantities, case corrosion rates, pollutant leach rates, and transport (dispersal paths in the soil) are acquired. In the interim, treatment and disposal of waste lithium batteries as an environmentally hazardous waste would be prudent.

## SECTION 4

### IDENTIFICATION OF LITHIUM BATTERY MATERIALS

Initially, a survey of battery manufacturers was conducted to determine the types of lithium anode battery systems currently being produced and distributed in this country. The results of this survey are presented in Table 4-1. At least 18 companies are currently producing or marketing lithium batteries. (Companies which produce batteries for specialized applications, or those which custom design batteries according to customer specifications, may not be included in the table.) Lithium battery systems discussed in this report are: lithium-sulfur dioxide, lithium-thionyl chloride, lithium-polycarbon monofluoride, lithium-manganese dioxide, lithium-iodine, lithium-iron sulfide, lithium-copper oxide, lithium-silver chromate, and lithium-vanadium pentoxide. Lithium battery systems which are in production but not discussed, due to lack of data, are the lithium-sulfuryl chloride and lithium-lead bismuthate systems.

Table 4-2 lists the lithium battery systems investigated during this study. Of these, a limited number are currently available for over-the-counter purchase, but they represent a very small percentage of total battery sales. Lithium batteries currently available for over-the-counter purchase are: lithium-polycarbon monofluoride, lithium-iron sulfide, and lithium-manganese dioxide. Lithium-copper oxide, lithium-iodine and lithium-silver chromate cells were not available for over-the-counter purchase, but are utilized by consumers in specialty applications, such as consumer electronics, heart pacemakers, and fire alarm equipment. The lithium-sulfur dioxide, lithium-thionyl chloride and lithium-vanadium pentoxide systems are used primarily for military and industrial applications and are frequently designed and manufactured according to customer specifications.

To fully assess lithium battery safety and environmental hazards, it was necessary to identify 1) hazardous chemicals and compounds found in waste lithium cells, and 2) any new products created as the result of disposal processes.

The common component of all electrochemical systems investigated in this study is the lithium which is used to construct the anodes. Lithium is the lightest and least reactive alkali metal and is, in fact, the lightest of all solid elements. Of the alkali metals, it possesses the largest negative

TABLE 4-1 LITHIUM BATTERY MANUFACTURERS

Manufacturer	Type(s)	Size(s)	Rated Cell Voltages(s)	Applications
1. Altus Corporation San Jose, CA	Lithium-thionyl chloride (Li/SOCl <sub>2</sub> )	Custom	3.6V	Military, CMOS * Circuits, Industrial
2. Battery Engineering Newton, MA	Li/SOCl <sub>2</sub> Lithium-sulfur dioxide (Li/SO <sub>2</sub> )	AA,C,DD,Custom	3.6V	Military, Industrial
3. Catalyst Research Baltimore, MD	Lithium-iodine (Li/I)	Button, Prismatic <sup>1</sup>	2.8V	Electronic Circuits, Cardiac Pace-makers, Military
4. Duracell International Elmsford, NY	Li/SO <sub>2</sub> Lithium-manganese dioxide (Li/MnO <sub>2</sub> ) Li/I	C,D, Cylindrical cells	3.0V 3.0V 3.0V 1.9V	Military, Industrial Consumer Products (Li/MnO, Li/I)
5. Eagle-Picher Joplin, Missouri	Li/SOCl <sub>2</sub> Carbon-monofluoride (Li/CF) Li/MnO <sub>2</sub>	1/2AA, AA, A, C, D, DD, Custom, Prismatic	3.6V 2.8V 3.0V	Electronic Circuitry, Military, Industrial, Consumers Products
6. Electrochem Industries Clarence, NY	Li/SOCl <sub>2</sub> (Bromine Complex)	Button, 1/2AA, AA, 2/3A 2/3C, 1/2C, D, DD Custom	3.9V	Electronic Circuits, Military, Industrial
7. General Electric Gainesville, FL	Li/MnO <sub>2</sub>	C, D	3.0	
8. GTE Waltham, MA	Li/SOCl <sub>2</sub>	1/2AA, AA, C, D, DD Prismatic Custom	3.6V	Military, Electronic Circuits, Industrial
9. Honeywell Horsham, PA	Lithium-sulfuryl chloride, (Li/SO <sub>2</sub> Cl <sub>2</sub> ) Li/SOCl <sub>2</sub> , Li/SO <sub>2</sub> , Lithium-vanadium pentoxide (Li/V <sub>2</sub> O <sub>5</sub> )	C, D, DD, Prismatic, Custom	2.9V 3.6V 3.4V	Military, Industrial, Medical
10. Lockheed Palo Alto, CA	Lithium-silver oxide (Li/Ag <sub>2</sub> O)	Custom	-	Military, Space rocket propulsion applications
11. Matsushita (Panasonic) Secaucus, NJ	Li/CF, Li/MnO <sub>2</sub>	Paper sizes, Button 1/2A, 2/3A, C, Cylindrical	3.0V 6.0V	Industrial, Electronic Circuits, Consumer Products
12. Power Conversion Elmwood Park, NJ	Li/SO <sub>2</sub> , Li/MnO <sub>2</sub> Li/SOCl <sub>2</sub> , Li/CF <sup>2</sup>	1/2AA, AA, 1/2A 2/3A, 3/4C, C, 1 1/4C, C	2.8V 3.0V 3.4V	Military, Consumer, Medical
13. Ray-O-Vac Madison, WI	Li/MnO <sub>2</sub> , Li/CF	Button, C, D	2.9V 3.6V	Consumer, Medical

\*CMOS - Complementary Metal Oxide Semiconductor

1

Includes bathtub shapes and flat cells

TABLE 4-1 (Concluded)

Manufacturer	Type(s)	Size(s)	Rated Cell Voltages(s)	Applications
14. SAFT Valdosta, GA	Li/SOCl <sub>2</sub> , Li/MnO Lithium-copper oxide (Li/CuO) Lithium-silver chromate (Li/Ag <sub>2</sub> CrO <sub>4</sub> ) Lithium-lead bismuthate (Li/Bi <sub>2</sub> Pb <sub>2</sub> O <sub>5</sub> )	Button, 1/2AA, AA Prismatic <sup>1</sup>	3.5V 3.0V 1.5V	Military (Li/SOCl <sub>2</sub> ), Medical (Li/Ag <sub>2</sub> CrO <sub>4</sub> ), Electronic Circuits, Industrial, Consumer Products (Li/Bi <sub>2</sub> Pb <sub>2</sub> O <sub>5</sub> , Li/CuO, Li/MnO <sub>2</sub> )
15. Sanyo Little Ferry, NJ	Li/MnO <sub>2</sub>	Y, N, 2N, C, D, Button, Prismatic	3.0V 6.0V	Consumer, Industrial
16. Tadiran-Israel Plainview, NY	Li/SOCl <sub>2</sub>	1/2AA, C, D, AA	3.6V	Military, Electronic Circuits
17. Union Carbide New York, NY	Li/MnO <sub>2</sub> , Li/CF Lithium-iron sulfide (Li/FeS)	Button	1.5V	Industrial, Consumer
18. Wilson Greatbatch Clarence, NY	Li/I	Button, Prismatic	2.8V	Medical

\* Complimentary Metal Oxide Semiconductor

<sup>1</sup> Includes bathtub shapes and flat cells

TABLE 4-2 HAZARD CHARACTERISTICS OF LITHIUM BATTERY MATERIALS

System	Material	Phase*	NFPA Classification**			Toxicity Rating <sup>+</sup>	Comments
		20°C: 1 atm	Health	Flamm.	React.		
Li/SO <sub>2</sub>	Sulfur Dioxide	G	2	0	0	High	Irritating gas. Toxic in high concentration.
	Acetonitrile	L	3	3	2	Moderate	Dangerous when exposed to heat or flame.
	Propylene Carbonate	L	1	1	0	None	Slight fire hazard.
	Lithium Bromide	S	NA	NA	NA	Unknown	
Li/SOCl <sub>2</sub>	Thionyl Chloride	L	NA	NA	NA	High	Corrosive. Emits toxic fumes when exposed to air.
	Lithium Tetrachloraluminate	S	NA	NA	NA	NA	
	Aluminum Chloride	S	3	0	2	Moderate	Exposure to moisture produces toxic or corrosive fumes.
	Lithium Sulfide	S	NA	NA	NA	Unknown	
	Sulfur Dioxide	G	2	0	0	High	Irritating gas. Toxic in high concentrations.
	Lithium Chloride	S	NA	NA	NA	Moderate	
	Sulfur	S	2	1	0	Very Low	Emits toxic fumes during burning.
Li/(CF) <sub>x</sub>	Carbon Monofluoride	S	NA	NA	NA	NA	
	Methyl Acetate	L	1	3	0	Moderate	Fire/explosion hazard when exposed to heat.
	Lithium Hexafluoroarsenate	S	NA	NA	NA	NA	
	Dimethyl Sulfite	L	NA	NA	NA	Unknown	Emits toxic fumes upon heating.
	Methyl Formate	L	2	4	1	Moderate	Fire/Explosion/Toxic fume hazards when exposed to heat.
	Lithium Fluoride	S	NA	NA	NA	High	High toxicity via ingestion.
Li/MnO <sub>2</sub>	Manganese Dioxide	S	NA	NA	NA	High	High toxicity via intravenous route.
	Lithium Perchlorate	S	NA	NA	NA	Unknown	Irritant
	Propylene Carbonate	L	1	1	0	None	Slight fire hazard.
	1,2-Dimethoxyethane	L	2	2	0	Unknown	Moderate fire/explosion hazard when exposed to heat
	Methyl Acetate	L	1	3	0	Moderate	Fire/explosion hazard when exposed to heat.
	1,2-Propanediol	L	0	1	0	None	Low fire/explosion hazard when exposed to heat.
	Carbon Dioxide	G	NA	NA	NA	Asphyxiant	Asphyxiating gas.

<sup>+</sup>Re  
NA

ce 4  
a Not Available

\* G = Gas; L = Liquid; S = Solid

\*\* NFPA classifications - Health, Flammability and Reactivity (stability).  
Numbers from 0 to 4 e increasing hazard.

TABLE 4-2 (Continued)

System	Material	Phase	NFPA Hazard Classification				Comments
		20°C: 1 atm	Health	Flamm.	React.	Toxicity Rating	
II	Li/I	Iodine	S	NA	NA	High	Emits toxic fumes when heated.
		Poly-2-Vinylpyridin	L	NA	NA	Unknown	
		Zirconium	S	NA	NA	Unknown	
		Lithium Iodine	S	NA	NA	NA	
	Li/FeS	Iron Sulfide	S	NA	NA	Unknown	
		Tetrahydrofuran	L	2	3	0	Fire/explosion hazard.
		1,2-Dimethoxyethane	L	2	2	0	Moderate fire/explosion hazard when exposed to heat.
		Lithium Perchlorate	S	NA	NA	Unknown	Irritant
		Propylene Carbonate	L	1	1	0	Slight fire hazard.
		Butyrolactone	L	0	1	0	Slight fire hazard.
		Lithium Sulfide	S	NA	NA	Unknown	
II	Li/CuO	Copper Oxide	S	NA	NA	Unknown	Moderate fire/explosion hazard when exposed to heat.
		Lithium Perchlorate	S	NA	NA	Unknown	Irritant
	Li/Ag <sub>2</sub> CrO <sub>4</sub>	Silver Chromate	S	NA	NA	Unknown	
		Lithium Perchlorate	S	NA	NA	Unknown	Irritant
		Propylene Carbonate	L	1	1	0	Slight fire hazard.
		Lithium Chromate	S	NA	NA	Unknown	Slight fire hazard.
	Li/V <sub>2</sub> O <sub>5</sub>	Vanadium Pentoxide	S	NA	NA	High	Dust has high toxicity properties via inhalation. Also toxic via injection.
		Nitromethane	L	1	3	4	Fire/explosion hazard when exposed to heat
		Ethylene Carbonate	S	2	1	1	Slight fire hazard.
		Lithium Perchlorate	S	NA	NA	Unknown	Irritant
		Aluminum Chloride	S	3	0	2	Exposure to moisture produces toxic or corrosive fumes.
		Lithium Hexafluoroarsenate	S	NA	NA	NA	
		Lithium Tetrafluoroborate	S	NA	NA	NA	
		Methyl Formate	L	2	4	1	Fire/Explosion/Toxic fume hazards when exposed to heat.
		Lithium Vanadium Pentoxide	S	NA	NA	NA	

electrode potential. This makes it ideal for use in high energy density battery systems. Lithium melts at approximately 179°C and will ignite in air near that temperature. Traditional fire suppression agents may not be entirely effective against lithium and in some cases will intensify the fire. Lith-X, a graphite-based, dry chemical fire suppression agent, is recommended for the extinguishment of lithium fires. However, extinguishment becomes more complicated 1) if the lithium is mixed with Class A materials (such as would be found in typical rubbish) which require cooling together with fire suppression; or 2) if the burning lithium surface is inaccessible to direct application of the suppression agent. The difficulty in extinguishing the fire is directly related to the amount of lithium involved and ignited. However, for most applications, the amount of lithium used in the production of a cell is extremely small, generally less than 1/2 gram.

Lithium is extremely reactive with water, nitrogen (at high temperatures), carbon dioxide, acids, or oxidizing agents. Lithium reacts with water to form lithium hydroxide (LiOH) and hydrogen (H<sub>2</sub>). The LiOH by-product of this reaction is both caustic and toxic. Hydrogen is explosive in air at concentrations of 4 to 75 percent by volume. However, no instance of ignition of either lithium metal or hydrogen gas as the result of the lithium-water reaction was noted in the literature reviewed for this study. Finally, an explosion hazard can exist when lithium is used to form compounds with heavy metals such as silver oxide, silver chloride, mercury oxide, etc.

Basic cell components and electrochemical reaction by-products for the various lithium cells were identified using published battery research data and manufacturers' product bulletins. Existing safety and toxicity data<sup>(3-8)</sup> were consulted to determine the hazard characteristics of these materials. These data are presented in Table 4-2. Table 4-2 shows the material phase (gas, liquid, or solid) at 20°C and 1 atmosphere pressure, its National Fire Protection Association (NFPA) Hazard Classification<sup>(3)</sup>, and its Sax Toxicity Rating<sup>(4)</sup>.

The identification of by-products created as the result of disposal processes required making the assumption that unprocessed<sup>†</sup> waste lithium batteries are placed in an ordinary land disposal area (either above or below ground). Cells assigned to these areas, even if unopened, will eventually release their contents

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<sup>†</sup> without benefit of neutralization



to the surroundings. When this occurs, the released chemicals and compounds become free to react with the environment (soil, water, air) and produce additional compounds which may pose new environmental and safety threats. To assess this problem, available toxicity data<sup>(3-8)</sup> were consulted to determine reaction products between lithium battery components and these materials. Data identifying the by-products of reactions between lithium battery materials and soils were not available. Reactions between identified lithium battery compounds and air were predicted upon the existence of moisture, and are, therefore, equivalent to those reactions solely involving water.

The effect of water upon exposed lithium battery components is also of interest because precipitation or subsurface waters will eventually combine with lithium battery components to produce leachates which could enter water supplies. According to sources surveyed during this study<sup>(3-8)</sup>, a number of lithium battery materials react with water to produce hazardous elements. These materials, and their reaction products are presented in Table 4-3.

Spontaneous heating of trash often occurs at land disposal areas as the result of the biochemical decay of organic matter. For this reason, it was desirable to determine the effects of elevated temperatures upon lithium battery chemicals and compounds. Lithium battery components which produce hazardous substances when heated are also presented in Table 4-3. Components which do not produce hazardous by-products when exposed to either water or heat are not included in this table.

#### LITHIUM-SULFUR DIOXIDE ( $\text{Li}/\text{SO}_2$ )

Lithium-sulfur dioxide ( $\text{Li}/\text{SO}_2$ ) battery systems have been commercially available for approximately ten years. The system has undergone various evolutionary changes precipitated by valid concerns regarding its electrochemical stability. Basic components of  $\text{Li}/\text{SO}_2$  cells are the lithium anode, a polytetrafluoroethylene (TEFLON)-bonded carbon cathode on an expanded aluminum screen, and an organic electrolyte. The electrolyte can be either acetonitrile (AN) or a propylene carbonate (PC) solvent containing a salt such as lithium bromide ( $\text{LiBr}$ ) or lithium hexafluoroarsenate ( $\text{LiAsF}_6$ ); the AN- $\text{LiBr}$  solvent-salt combination is more commonly used. The active cathode material, sulfur dioxide ( $\text{SO}_2$ ), is included in the electrolyte. The concentration of  $\text{SO}_2$  in the electrolyte attenuates as the cell discharges. Standard cells utilize an electrolyte/depolarizer

TABLE 4-3 COMPONENTS OF LITHIUM BATTERY SYSTEMS WHICH REACT WITH WATER OR HEAT<sup>†</sup>

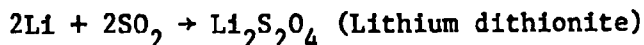
Cell Type	Component	Products of Reaction with H <sub>2</sub> O	Products of Reaction with Heat
Li/SO <sub>2</sub>	<u>Basic Components</u>		
	Sulfur Dioxide (SO <sub>2</sub> )	Sulfuric acid (H <sub>2</sub> SO <sub>4</sub> )	Exothermic reactions, Hydrogen cyanide gas
	Acetonitrile (Methyl cyanide-CH <sub>3</sub> CN)	Cyanides	
Li/SOCl <sub>2</sub>	<u>Basic Components</u>		
	Thionyl Chloride (SOCl <sub>2</sub> )	Hydrogen Chloride(HCl), Sulfur Dioxide(SO <sub>2</sub> )	Sulfur dioxide, Sulfur chloride
	Aluminum Chloride (AlCl <sub>3</sub> )	Violent exothermic reactions, Hydrogen chloride (HCl)	Chlorides
	<u>Electrochemical Reaction By-products</u>		
	Lithium Sulfide (Li <sub>2</sub> S)	Hydrogen sulfide (H <sub>2</sub> S)	SO <sub>x</sub> gases
	Sulfur Dioxide (SO <sub>2</sub> )	Sulfuric acid (H <sub>2</sub> SO <sub>4</sub> ) Sulfurous Acid (H <sub>2</sub> SO <sub>3</sub> )	
	Sulfur (S)		Exothermic reactions, Sulfur dioxide
Li/(CF) <sub>x</sub>	<u>Basic Components</u>		
	Methyl Acetate (CH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub> )		Exothermic reactions
	Dimethyl Sulfite ((CH <sub>3</sub> ) <sub>2</sub> SO <sub>3</sub> )	Sulfur dioxide	
	Methyl Formate (HCOOCH <sub>3</sub> )		Exothermic reactions
Li/MnO <sub>2</sub>	<u>Basic Components</u>		
	Manganese Dioxide (MnO <sub>2</sub> )		Exothermic reactions
	Lithium Perchlorate (LiClO <sub>4</sub> )		Chlorides (LiCl)
	1,2-Dimethoxyethane(CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> )		Exothermic reactions
	Methyl Acetate (CH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub> )		Exothermic reactions
	<u>Electrochemical Reaction By-products</u>		
	1,2 Propanediol (CH <sub>2</sub> OHCH <sub>2</sub> OHCH <sub>3</sub> )		Exothermic reactions
Li/I	<u>Basic Components</u>		
	Poly-2-vinylpyridine [(-CH(C <sub>5</sub> H <sub>4</sub> N)-CH <sub>2</sub> -) <sub>7</sub> ]		Exothermic reactions, cyanides
Li/Fes	<u>Basic Components</u>		
	Tetrahydrofuran (OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> )		Peroxides
	1,2-Dimethoxyethane (CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> )		Exothermic reactions
	Lithium Perchlorate (LiClO <sub>4</sub> )		Chlorides (LiCl)
	<u>Electrochemical Reaction By-products</u>		
	Lithium Sulfide (Li <sub>2</sub> S)	Hydrogen Sulfide (H <sub>2</sub> S)	SO <sub>x</sub> gases

TABLE 4-3 (Concluded)

Cell Type	Component	Products of Reaction with H <sub>2</sub> O	Products of Reaction with Heat
Li/CuO	<u>Basic Components</u>		
	1,2-Dimethoxyethane (CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> )		Exothermic reactions
	Lithium Perchlorate (LiClO <sub>4</sub> )		Chlorides (LiCl)
Li/Ag <sub>2</sub> CrO <sub>4</sub>	<u>Basic Components</u>		
	Lithium Perchlorate (LiClO <sub>4</sub> )		Chlorides (LiCl)
	<u>Electrochemical Reaction By-products</u>		
	Lithium Chromate (LiCrO <sub>4</sub> )		Exothermic reactions
Li/V <sub>2</sub> O <sub>5</sub>	<u>Basic Components</u>		
	Nitromethane (CH <sub>3</sub> NO <sub>2</sub> )		Exothermic reactions
	Ethylene Carbonate (C <sub>3</sub> H <sub>4</sub> O <sub>3</sub> )		Exothermic reactions
	Lithium Perchlorate (LiClO <sub>4</sub> )		Chlorides (LiCl)
	Aluminum Chloride (AlCl <sub>3</sub> )	Violent exothermic reactions, Hydrogen chloride (HCl).	Chlorides (LiCl)
	Methyl Formate (HCOOCH <sub>3</sub> )		Exothermic reactions

combination consisting (approximately) of 70% SO<sub>2</sub> (liquid) + 10% AN + 20% LiBr by weight<sup>(10,11)</sup>. Cells which use a propylene carbonate (PC) solvent have electrolyte/depolarizer combinations of 70% SO<sub>2</sub> + 20% AN/PC<sup>†</sup> + 10% LiBr by weight. When LiAsF<sub>6</sub> is employed as the electrolyte salt, the electrolyte/depolarizer combination is likely to be 70% SO<sub>2</sub> + 21% AN + 9% LiAsF<sub>6</sub> by weight. A typical cell is constructed using a "jelly roll" configuration (see Figure 4-1). This involves creating a "sandwich" of the anode material (Li), polypropylene separator, and carbon cathode/current collector. The "sandwich" is then spirally wound and inserted in a steel can with the lithium side in contact with the internal wall of the can. Rupture vents or pressure-relieving diaphragms are incorporated in the design of these batteries as safety features.

The cell accepted basic reaction is<sup>(12)</sup>:



In addition to the production of lithium dithionite, Li/SO<sub>2</sub> cells have been known to produce methane (CH<sub>4</sub>), lithium cyanide (LiCN), and B-amino-n-butyronitrile under certain circumstances<sup>(12,13)</sup>. On occasion, usually under conditions of thermal stress, either internal or external in origin, Li/SO<sub>2</sub> cells will vent SO<sub>2</sub> to the surroundings<sup>††</sup>. SO<sub>2</sub> is an irritating gas in concentrations of 6-12 ppm<sup>(9)</sup> and requires 400-500 ppm to be considered life-threatening. It can react with water and steam to produce sulfuric (H<sub>2</sub>SO<sub>4</sub>) and sulfurous (H<sub>2</sub>SO<sub>3</sub>) acids. The acetonitrile used in these cells is both toxic and flammable\*. Acetonitrile can react explosively with sulfuric acid, which could be produced by the H<sub>2</sub>O-SO<sub>2</sub> reaction in or near a breached cell. When heated to decomposition acetonitrile will also emit toxic cyanide fumes.

#### LITHIUM-THIONYL CHLORIDE (Li/SOCl<sub>2</sub>)

The lithium-thionyl chloride (Li/SOCl<sub>2</sub>) cell has the highest energy density of all commercially available lithium anode battery systems. The cell consists of a lithium anode, a TEFLON-bonded carbon cathode, a nonwoven or felted fiberglass separator, and the inorganic liquid SOCl<sub>2</sub> as the electrolyte solvent and

<sup>†</sup> AN/PC in a 3:1 combination

<sup>††</sup> The cell is initially pressurized to 3-4 atmospheres by the SO<sub>2</sub> contained in its electrolyte.

\* Department of Transportation (DOT) definition of flammable and combustible

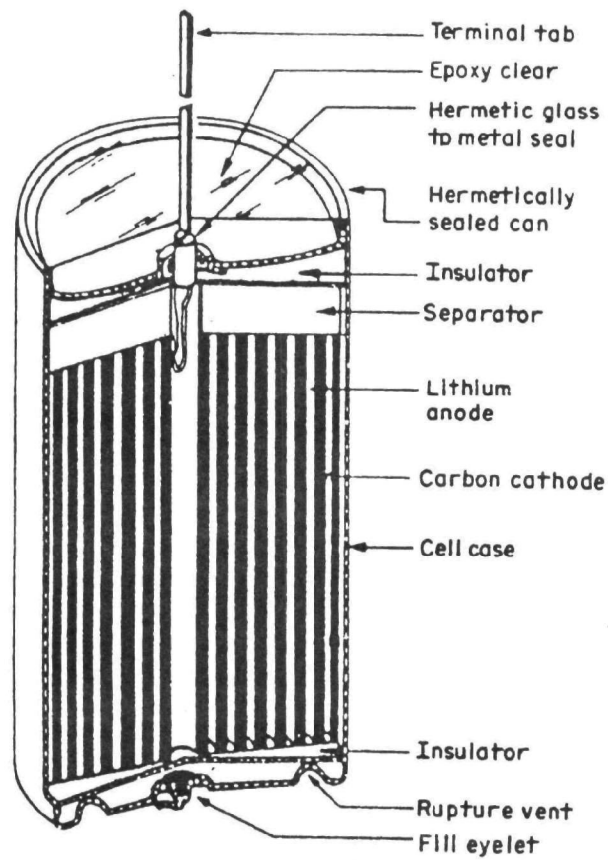
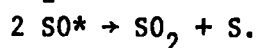
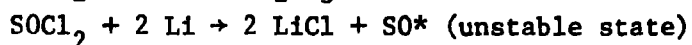
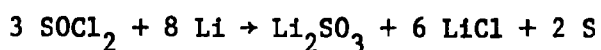


Figure 4-1 Internal structure of a lithium-sulfur dioxide cell  
(Duracell International, Inc.) (ref. 11)

active cathode material. Included in the thionyl chloride is lithium tetrachloroaluminate ( $\text{LiAlCl}_4$ ), or one of two specially prepared salts of chemical formulation-- $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$  and  $\text{Li}_2\text{O}(\text{AlCl}_3)_2$ <sup>(14,15)</sup>. Cells can be constructed either using a "jelly roll" configuration similar to that used for  $\text{Li}/\text{SO}_2$  cells (Figure 4-1) or employing a cylindrical, highly porous carbon cathode, containing the electrolyte, surrounded by a current collector (Figure 4-2). Thionyl chloride cells utilize low pressure vents and fuses to prevent conditions which might lead to thermal runaway reactions. The most commonly cited cell reaction<sup>(16)</sup> is:

$$2 \text{SOCl}_2 + 4 \text{Li} \rightarrow 4 \text{LiCl} + \text{SO}_2 + \text{S},$$
although two others have been proposed<sup>(17)</sup>, namely:

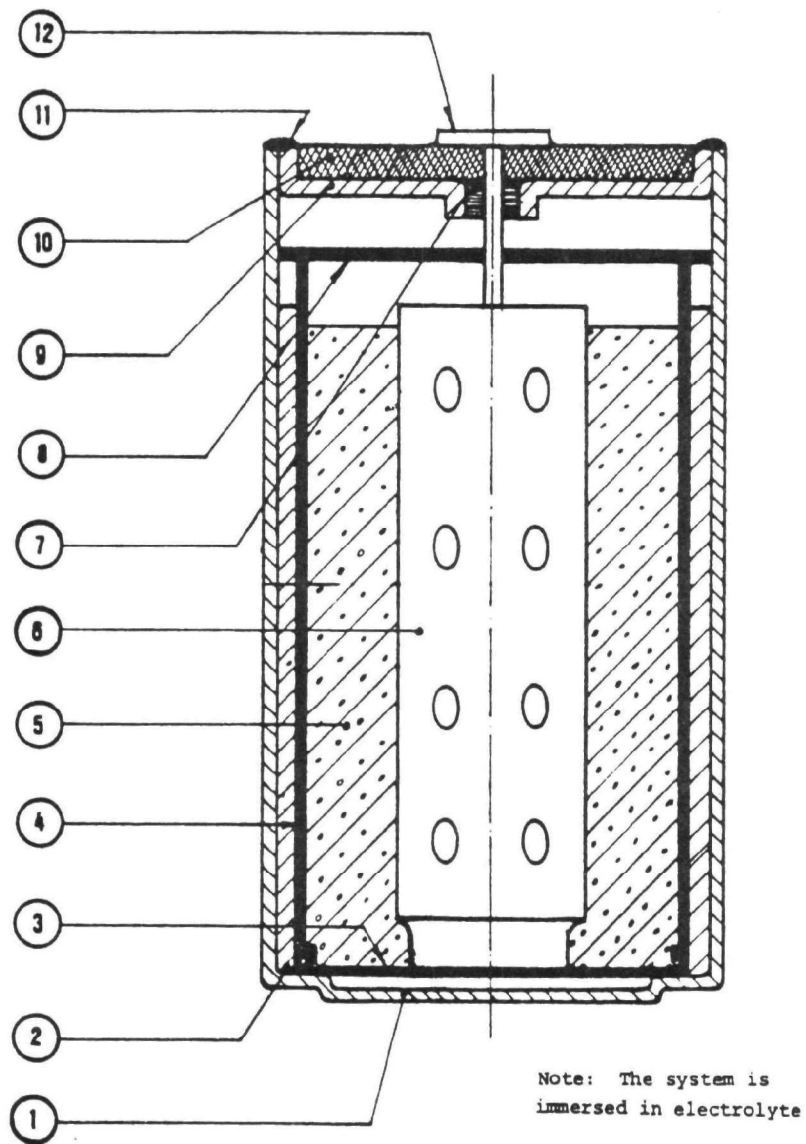


Thionyl chloride is more toxic than sulfur dioxide and is classified as a corrosive liquid. In the presence of moisture, it violently decomposes into hydrogen chloride and sulfur dioxide.

The production of sulfur dioxide and sulfur during the electrochemical process is noteworthy because: 1) sulfur dioxide produces sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and sulfurous acid ( $\text{H}_2\text{SO}_3$ ) when it contacts water and 2) the mixture of sulfur and molten lithium is potentially explosive<sup>(18)</sup>.

#### LITHIUM-POLYCARBON MONOFLUORIDE ( $\text{Li}/(\text{CF})_x$ )

The lithium-polycarbon monofluoride ( $\text{Li}/(\text{CF})_x$ ) cell was developed in 1968 and appears to be an attractive system for many low-current consumer applications. The  $\text{Li}/(\text{CF})_x$  cell consists of a solid lithium foil anode rolled onto a nickel collector; a TEFLON-bonded polycarbon monofluoride cathode; and an organic electrolyte composed of lithium hexafluoroarsenate ( $\text{LiAsF}_6$ ) dissolved in either methyl formate ( $\text{HCOOCH}_3$ ), methylacetate ( $\text{CH}_3\text{CO}_2\text{C}_{10}\text{H}_{19}$ ), or dimethylsulfite ( $(\text{CH}_3)_2\text{SO}_3$ )<sup>(19,20)</sup>. Cylindrical cells can be constructed using the "jelly roll" configuration, with polypropylene as the separator. In button cells, the anode and cathode materials are formed into disks which are separated by another disk of polypropylene.



KEY:

- |                      |                               |
|----------------------|-------------------------------|
| 1 - CAN              | 7 - GLASS-TO-METAL SEAL       |
| 2 - ANODE            | 8 - TOP INSULATOR             |
| 3 - BOTTOM INSULATOR | 9 - COVER                     |
| 4 - SEPARATOR        | 10 - EPOXY FILLING            |
| 5 - CATHODE          | 11 - HERMETICALLY WELDED SEAM |
| 6 - COLLECTOR        | 12 - POSITIVE TERMINAL        |

Figure 4-2 Lithium-thionyl chloride cell (Tadiran Israel Electronics Industries, Ltd.) (ref. 32)

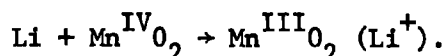
The cell reaction is:



Resultant products are carbon and lithium fluoride, which are formed without the production of gases or heat in low rate cells. Larger, high rate cells must be vented to reduce the probability of explosion<sup>(18)</sup>. Lithium fluoride is considered to be highly toxic<sup>(4)</sup>. Other materials of interest are the solvents used for electrolytes. Dimethyl sulfite is an irritant which, upon heating, emits toxic fumes of  $SO_x$ ; it can also react with water or steam to produce sulfur dioxide. Methyl formate and methyl acetate are flammable<sup>†</sup> liquids.

#### LITHIUM-MANGANESE DIOXIDE (Li/MnO<sub>2</sub>)

High energy density and economical fabrication are the positive aspects of lithium-manganese dioxide (Li/MnO<sub>2</sub>) battery systems. These systems are very attractive for consumer applications. Li/MnO<sub>2</sub> cells utilize a lithium anode, a manganese dioxide (MnO<sub>2</sub>) cathode, and an organic electrolyte in various configurations<sup>(21)</sup>. A typical electrolyte consists of a mixture of two organic solvents, propylene carbonate and 1,2-dimethoxyethane (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), to which lithium perchlorate (LiClO<sub>4</sub>) has been added. Separators of polypropylene are used. Cylindrical cells are constructed using either the "jelly roll" or inside-out (external cathode, see Figure 4-3) configurations. Prismatic and button cells are also available. The cell reaction is<sup>(22)</sup>:



By-products of the electrochemical reaction have been suggested to be 1,2-propanediol (CH<sub>2</sub>OHCHOHCH<sub>3</sub>) and carbon dioxide<sup>(22)</sup>. The propanediol can further react with the lithium to produce lithium oxide and hydrogen or it can be absorbed by the MnO<sub>2</sub> and be oxidized to propylaldehyde and water.

Manganese dioxide is considered to be highly toxic if ingested<sup>(4)</sup>. Both propylene carbonate and 1,2-dimethoxyethane are combustible.<sup>†</sup>

#### LITHIUM-IODINE (Li/I-PVP)

Various designs using this chemistry are currently on the market, primarily for use in cardiac pacemaker applications. A typical lithium-iodine (Li/I) cell will consist of a lithium anode, a cathode/depolarizer composed of iodine and

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<sup>†</sup> DOT definitions of flammable and combustible



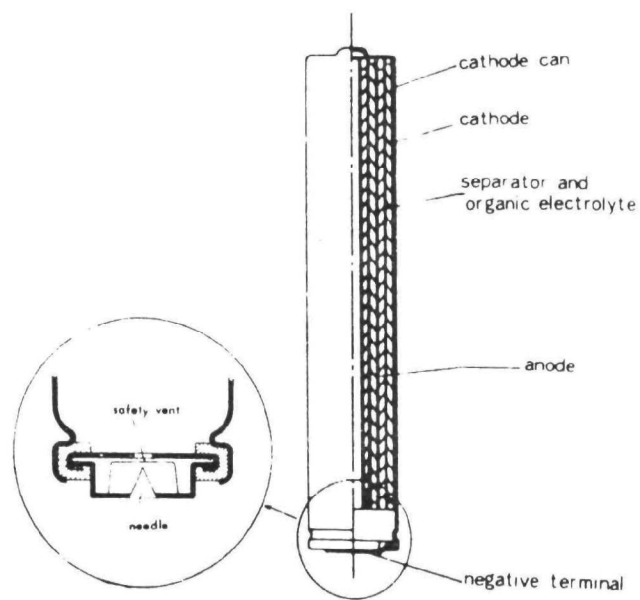
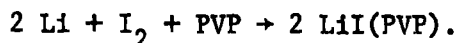


Figure 4-3 Cross-sectional view of cylindrical  
inside-out Li/MnO<sub>2</sub> cell  
(Sanyo Electric Company, Ltd.)(ref. 21)

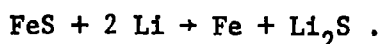
polyvinylpyridine (PVP), and an electrolyte/separator of solid LiI which is formed when the PVP is added prior to sealing the cell. Zirconium (Zr) serves as the current collector and holder for the anode<sup>(23)</sup>. The cell reaction is:



During service, the LiI electrolyte/separator increases in size as the cell discharges. Cells are hermetically sealed and do not employ venting mechanisms. Both iodine and zirconium are slightly radioactive, and iodine has a high toxicity rating according to Sax<sup>(4)</sup>.

#### LITHIUM-IRON SULFIDE (Li/FeS)

Small button-type 1.5 volt organic electrolyte Li/FeS cells are currently produced by Union Carbide. The components of these cells, according to the product bulletin, include a lithium anode; an FeS cathode and a separator/electrolyte of unspecified composition<sup>(24)</sup>. Experimental cells developed by Uetani<sup>(25)</sup> of Hitachi Maxell Ltd. utilized organic electrolytes of lithium perchlorate plus one or more of the following: propylene carbonate,  $\gamma$ -butyrolactone, tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME). The cell reaction is:



The lithium sulfide ( $\text{Li}_2\text{S}$ ) produced during the electrochemical reaction may yield hydrogen sulfide when it contacts water. When heated,  $\text{Li}_2\text{S}$  will emit  $\text{SO}_x$  gases as it decomposes. Propylene carbonate,  $\gamma$ -butyrolactone, tetrahydrofuran and 1,2-dimethoxyethane are combustible<sup>†</sup> liquids; the tetrahydrofuran being extremely flammable.

#### LITHIUM COPPER-OXIDE (Li/CuO)

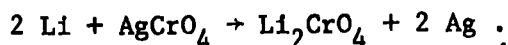
The Li/CuO cell is in limited production and as a result there is very little information regarding its composition. However, the Li/CuO cell should be similar in construction to the Li/FeS system.. Basic constituents are a lithium anode, copper oxide cathode plus an organic electrolyte. The electrolyte used is probably 1,2-dimethoxyethane (DME) solvent to which lithium perchlorate has been added. The 1,2-dimethoxyethane is a combustible<sup>†</sup> liquid. Lithium perchlorate may emit chloride fumes when exposed to elevated temperatures

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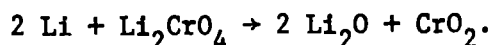
<sup>†</sup> DOT definitions

#### LITHIUM-SILVER CHROMATE ( $\text{Li}/\text{Ag}_2\text{CrO}_4$ )

The lithium-silver chromate ( $\text{Li}/\text{Ag}_2\text{CrO}_4$ ) cell consists of a lithium anode a silver chromate/acetylene black cathode, and an organic electrolyte. One such cell developed by SAFT utilizes an organic electrolyte which is prepared by dissolving lithium perchlorate in propylene carbonate. The overall cell reaction has been reported to be<sup>(26,27)</sup>:



A secondary reaction has been reported as<sup>(26)</sup>:

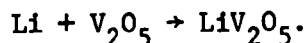


Although the exact cell "recipe" could not be determined from the product literature, the hazards associated with these cells should be similar to those of the lithium-iron sulfide and copper oxide systems in which the primary hazard(s) are due to the use of flammable and combustible electrolytes such as DME and tetrahydrofuran.

#### LITHIUM-VANADIUM PENTOXIDE ( $\text{Li}/\text{V}_2\text{O}_5$ )

The basic cell consists of: a lithium anode constructed by attaching lithium foil to a nickel screen current collector; an active cathode of vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) mixed with carbon pressed around a stainless steel grid; and an organic electrolyte. The electrolyte is produced by dissolving lithium hexafluoroarsenate ( $\text{LiAsF}_6$ ) and lithium tetrafluoroborate ( $\text{LiBF}_4$ ) salts in methyl formate ( $\text{HCOOCH}_3$ )<sup>(28-30)</sup> or methyl acetate ( $\text{CH}_3\text{CO}_2\text{CH}_3$ )<sup>(31)</sup>.

The accepted cell reaction for the  $\text{Li}/\text{LiBF}_4:\text{MA}/\text{V}_2\text{O}_5$  system has been reported to be<sup>(31)</sup>:



Hazards presented by  $\text{Li}/\text{V}_2\text{O}_5$  cells involve the methyl formate and methyl acetate solvents used in electrolytes. Both solvents are extremely flammable and represent an explosion hazard, if air is present in the cell.

## SECTION 5

### QUANTIFICATION OF WASTE LITHIUM BATTERY DISPOSAL HAZARDS

#### LITHIUM BATTERY WASTE DISPOSAL TECHNIQUES

The survey of battery industry disposal practices yielded only one organization, Battery Disposal Technology, Inc. located in Clarence, N.Y., which has as its sole function the disposition of waste lithium batteries. The facility is fully licensed and sanctioned by the U.S. Department of Transportation for receiving and handling lithium batteries. To effect disposal, this facility uses a process in which cell cases are breached and the contents neutralized in the same operation. To accomplish this, a rotating hammermill is used to crack cell cases in the presence of an unspecified aqueous spray which hydrolyzes the lithium and possibly other reactive components. After shredding, the reacted material is funneled through a screen into a holding tank where it is completely wetted with the same aqueous solution to insure that all materials are completely reacted. The wetted residues are subsequently pumped from the holding tank by a private contractor and, as a precautionary measure, deposited in a secured landfill. The Battery Disposal Technology facility processes all types of lithium cells but the bulk of those batteries processed are either lithium-sulfur dioxide or lithium-thionyl chloride.

Most manufacturers and large commercial and military users of lithium batteries who must dispose of the batteries do take specific precautions in the disposition process. Usually, this involves a neutralization procedure, such as breaching cell cases and reacting internal components with an aqueous solution, followed by disposal in a hazardous waste disposal facility. However, it is possible that manufacturers may not employ a neutralization procedure but instead seal waste lithium cells in containers (drums, barrels, etc.) which are then buried. The Environmental Protection Agency's classification of lithium batteries will determine future practices for these manufacturers.

#### CONVENTIONAL WASTE DISPOSAL TECHNIQUES

Conventional waste disposal operations are conducted in three phases: collection, processing (baling, compacting or shredding), and ultimate disposal via burial or incineration. The hazards associated with these various operations are summarized in Table 5-1.

TABLE 5-1 HAZARDS ASSOCIATED WITH DISPOSAL OPERATIONS

Operation	Hazardous Situation	Resultant Hazard
Collection	External short circuit	Explosion/fire/internal exothermic reactions
	Mechanical shock	
	- dropped	
	- thrown	
	Crushing of cell	
	- pickup vehicle compacting	Hazardous material release (cell breached)
	Foreign object penetration	
	- pickup vehicle compacting	
	Moisture intrusion	
	Mechanical shock	
Processing	- dropped	Explosion/fire/internal exothermic reactions/hazardous material release (cell breached)
	- thrown	
	Crushing of cell	
	- pickup vehicle compacting	
	Foreign object penetration	
	External short circuit	Hazardous gas release (cell intact)
	Mechanical shock	
	- dropped	
	- thrown	
	Moisture intrusion	
Disposal	External short circuit	Explosion/fire/internal exothermic reactions
	Crushing of cell	
	- shredding, compacting	
	Mechanical shock	
	- explosion in processing unit	
	Foreign object penetration	Hazardous material release (cell breached)
	Elevated temperature/fire	
	- heating or ignition by adjacent materials	
	- incineration	
	External short circuit	
Disposal	Elevated temperature/fire	Hazardous gas release (cell intact)
	External short circuit	
	Crushing of cell	
	- dump and filling operations	
	Moisture intrusion	
	Elevated temperature/fire	Hazardous material release (cell breached)
	Crushing of cell	
	- dump and filling operations	
	Elevated temperature/fire	
	External short circuit	
Disposal	Moisture intrusion	Hazardous gas release (cell intact)
	Elevated temperature/fire	
	- heating or ignition by adjacent materials	

During normal collections, waste batteries and cells may be subjected to 1) external short circuit - the result of electrical bridging of cell terminals by electrically conductive objects contained in the trash, 2) mechanical shock - caused by dropping or rough handling, 3) crushing - caused by the shredding or compacting operations of pickup vehicles, and 4) immersion in water or moist material. These situations could initiate hazardous incidents such as explosion, fire, internal exothermic reactions, and hazardous material releases. Internal exothermic reactions may result in elevated wall temperatures which could ignite adjacent refuse. Hazardous material releases may involve either the release of cell gases via operation of a safety vent (cell remains intact) or a serious failure of the cell container which potentially exposes all internals.

Processing operations may entail baling (or compacting), shredding, incineration, or a combination thereof. Baling/compacting operations may be performed on previously processed or unprocessed material, at the collection site or in a processing facility. Waste batteries processed through baling/compacting equipment may be subjected to: 1) external short circuit - as cells contact electrically conductive materials, 2) mechanical/shock - through the action of the compactor or an explosion in the processing unit, 3) crushing, 4) fire - initiated within the processing unit, and 5) foreign object penetration. During shredding operations, cells are crushed, their cases torn open, and contents released. In the shredder, exposed cell constituents may be subjected to spark ignition sources produced by the impact of shredding hammers striking metallic or abrasive waste material. The basic hazards encountered when processing waste lithium batteries will be the same as those associated with collection operations, i.e., explosion, fire, internal exothermic reactions, and hazardous material releases.

Strict environmental pollution regulation has forced the closing of many incineration operations in the United States. There are, however, some units still in operation. Unopened batteries and cells disposed of using incinerators may present an explosion hazard.

The final stage of the waste disposal process is the assignment of residual products to a permanent location. This is usually land burial or disposal at secured or sanitary landfills. During dumping and filling operations unopened

cells may be subjected to crushing and foreign object penetration. After completion of these operations, waste lithium cells are intermingled with assorted rubbish and may also be subjected to 1) immersion in water or moist material, and 2) elevated temperatures caused by the spontaneous heating of organic matter in the trash. The hazards associated with the final disposition of waste lithium cells are explosion, fire, release of hazardous material (including gases), and internal exothermic reactions.

#### CORRELATION OF ABUSE TEST DATA TO CONVENTIONAL WASTE DISPOSAL HAZARDS

The approach used in making determinations of hazards associated with the management of waste lithium batteries was the correlation of existing abuse test data to hazardous situations anticipated by conventional waste disposal operations. Available abuse test data on lithium batteries frequently duplicate hazards which are likely to occur during conventional waste disposal methods. By correlating abuse test data reported in the literature to those hazardous situations, hazard assessments were made. Correlations between abuse tests and hazardous situations are presented in Table 5-2. Numerous lithium battery safety tests were surveyed for applicability in making assessments. Seven tests were finally selected: 1) mechanical shock (drop test), 2) external short circuit, 3) immersion, 4) cell deformation (crush test), 5) elevated temperature, 6) incineration, and 7) foreign object penetration. Since data from many sources were reviewed, thereby yielding a variety of test procedures and test results, a set of minimum criteria for the conduct and evaluation of test data for each of the seven tests had to be established. The results are the generalized test procedures and evaluation criteria for each of the seven tests which are presented as Appendix A. The procedures for each of the outlined abuse tests are, for the most part, generalized composites of one or more existing tests. Evaluation criteria are stated in general terms since the bulk of existing abuse test data are reported that way. For example, quantities of either gases or electrolytes released during abuse tests were usually not defined, therefore no attempts were made to quantify such losses. Changes in the physical appearance of cells after test were also described in general terms such as cracked seals, crimp failures, or swollen and corroded cases.

TABLE 5-2 CORRELATION OF ABUSE TESTS TO DISPOSAL HAZARDS

<u>Hazard</u>	<u>Abuse Test</u>
1. Cell dropped, thrown or involved in explosion from adjacent cell	1. Mechanical shock
2. Terminals bridged via electrically conductive material	1. External short circuit
3. Cell submerged in water or moist material	1. Immersion test
4. Cell crushed or shredded	1. Cell deformation test
5. Cell exposed to heat or flame, including incineration	1. Elevated temperature test 2. Incineration test
6. Object penetrates cell casing	1. Foreign object penetration test



The basis for hazard assessments are the results of abuse tests on C- and D-cells (ANSI designations) since these data were more universally available. Unfortunately, the hazards associated with cells of different sizes may also be different and prevent the extrapolation of hazard potential between different battery sizes within a given chemistry. Abuse tests reviewed during this study are as follows.

#### MECHANICAL SHOCK

During collection and processing, waste lithium batteries may be dropped, thrown, or subjected to forces created by exploding waste material in close proximity. Because of this, efforts were made to determine the effects of mechanical shock upon lithium battery systems. Manufacturers such as Tadiran<sup>(32)</sup> and Power Conversion<sup>(33)</sup> adopted deceleration tests designed to conform with requirements set forth by the Federal Aviation Administration (FAA)<sup>(34)</sup> and the United States Army<sup>(35)</sup>. In these tests, lithium batteries are subjected to forces ranging from 100 to 1000 g's for durations of 0.5 to 23 ms. While the results of these tests provide useful information regarding the ability of internal components to withstand acceleration or deceleration, they provide no information on the cells' ability to withstand physical impact.

The Environmental Protection Agency (EPA) employs a Structural Integrity<sup>(36)</sup> Test for making determinations for hazardous waste. This test, while providing some impact data, appears to be much too lenient for making a determination as to the structural integrity of steel-clad battery cells. The EPA test involves impacting a cell 15 times with a 0.33 kg mass (.73 lb) from a height of 15.24 cm (6 in.). This is an insufficient challenge. However, drop tests such as those performed by Shah<sup>(37)</sup> and Bauman<sup>(38)</sup> do provide sufficient challenge for testing a cell's ability to withstand mechanical shock expected during waste collection and processing. Such tests duplicate the real-world situation in which a cell is either dropped or thrown from a height. The test by Shah requires that a cell be dropped from a height of 5 meters onto a concrete pad. Bauman used a height of 12.2 meters and a steel plate anvil instead of the concrete pad. The Bauman test is probably too severe since it is unlikely that a cell or battery would be dropped or thrown from a height of 12 meters or more during routine collection operations. Therefore, the Shah test (i.e., a drop

test from 5 meters) was used as the minimum requirement for evaluating the ability of a cell to withstand the mechanical shocks likely to be incurred during waste disposal operations.

Abuse test data reviewed during this study showed no instance of a commercial lithium battery or cell posing a hazard when dropped from a height of 5 meters or more. However, explosions did occur in several  $\text{Li/SO}_2$  specialty cells during the conduct of the drop tests performed by Shah.

#### SHORT CIRCUIT

When lithium cells and batteries are mixed together with rubbish and other trash, the possibility exists that contact with electrically conductive materials may cause short circuiting. It was, therefore, necessary to determine whether or not a cell could be short circuited without presenting a safety hazard. Several organizations, including Tadiran<sup>(32)</sup> and Factory Mutual<sup>(39)</sup> routinely use tests designed to assess the hazards associated with short circuiting of a cell or battery. Tests require bridging of battery terminals with a low-resistance electrical conductor, then observing the behavior for a period of time between 30 minutes and 24 hours.

Short circuit tests of lithium-thionyl chloride<sup>(14,40-45)</sup>, lithium-sulfur dioxide<sup>(33,46)</sup> and lithium-polycarbon monofluoride<sup>(19)</sup> revealed that these systems were affected to varying degrees by this condition. All of these batteries have vented under short circuit conditions, and explosions were documented for the lithium-thionyl chloride system<sup>(40,45)</sup>. These batteries have also successfully passed short circuit tests.

#### IMMERSION TESTS

Since waste lithium cells are likely to be disposed of along with moist materials or left in containers which collect water, it becomes necessary to define the hazards presented when these cells are immersed in water. This is particularly true of those cells which have vents or which are not hermetically sealed. Some cells contain components which are extremely reactive with water and the ability of the cell to withstand moisture intrusion is a significant protection requirement. Immersion tests in fresh and salt water have been performed by Brooks<sup>(33)</sup> on lithium sulfur dioxide batteries, and McCartney<sup>(40)</sup>

using lithium-thionyl chloride, with varying results. Immersion in salt water is the more severe test, primarily because of the possibility of accelerated corrosion of the cell case<sup>(40,47)</sup>.

None of the data reviewed gave indication of safety problems with any of the nine systems under study.

#### CELL DEFORMATION TEST (CRUSH TEST)

Compacting and baling operations could cause cell deformations which, in turn, may result in internal shorts or the release of toxic or flammable electrolyte. Internal shorts can cause exothermic reactions and explosions in certain types of lithium cells<sup>(18)</sup>. The cell deformation test involves the gradual crushing of the lower portion (bottom one-half, one-third or one-quarter) of a cell using a compression device (e.g., vise, mechanical clamps, etc.) while simultaneously monitoring the open circuit voltage and the cell wall temperature. The ability of the cell to withstand deformation without explosion or exothermic reaction was of primary interest.

With the exception of one lithium-sulfur dioxide cell which vented<sup>(33)</sup>, no particular safety problems were noted in the data reviewed.

#### ELEVATED TEMPERATURE/INCINERATION TESTS

There are essentially two scenarios. The first involves the situation in which waste lithium cells are subjected to elevated temperatures but not to the extent required for incineration. Spontaneous heating of organic material, the dumping of hot material onto the batteries or solar heating of closed trash containers are all possibilities. These exposures will in all likelihood produce temperatures somewhat lower than the melting point of lithium (179°C). Elevated temperature tests performed by Tadiran<sup>(32)</sup> (150°C for 3 hr), Babai and Zak<sup>(43)</sup> (63°C for 4 hr) and Rosansky and Watson<sup>(48)</sup> (71°C for 2 weeks and 54°C for 30 days) were examined.

The second scenario is that in which the lithium cell is incinerated. When lithium cells are included with other rubbish or trash, there exists the possibility that they can be either purposely or accidentally incinerated. Although most incineration equipment is designed to withstand minor explosions, the effect of a quantity of lithium cells exploding within such equipment has yet to be

determined. It would, therefore, be beneficial to know which cells represent an explosion hazard during incineration. To make this determination, a simple incineration test described in Table A-6 can be performed. What is required is the exposure of the cell to flame or high temperature<sup>(49)</sup> and maintaining this exposure until the cell is consumed. What is of interest is whether or not the cell explodes, produces toxic or corrosive gases, or significantly intensifies the fire. Taylor and McDonald<sup>(49)</sup> used both an explosionproof furnace at 540°C and direct flame for incineration tests.

The tests performed by Taylor and McDonald gave no indication of a significant safety hazard for lithium-sulfur dioxide cells in a furnace. However, incineration tests reported by Bajpai and Zalosh<sup>(39)</sup> indicate that lithium-polycarbon monofluoride batteries will burn violently and rocket under these conditions. Tests conducted at Factory Mutual for a private client demonstrate that the behavior of lithium batteries under elevated temperature and incineration conditions is a function of 1) cell packaging (soft-sided, steel can, single cell or multiple-cell arrangements, etc.), and 2) failure mode of cell casing (cells undergoing pressure relieving failures usually do not rocket or explode), as well as 3) its chemical composition.

#### FOREIGN OBJECT PENETRATION TEST

One of the more serious situations which might be encountered is that involving the penetration of a cell by an electrically conductive object. In this instance, there exists the potential for 1) release of flammable, toxic, or corrosive liquid and gas, or 2) internal short reactions (fire, explosion, etc.). Numerous foreign object penetration test procedures have been reported in the literature. Basically, these involve either boring<sup>(33)</sup> with a high-speed drill or puncturing<sup>(16,17,32,43,48)</sup> the case with manually- or mechanically-driven nails. In addition to determining if a fire or explosion hazard existed, checks of cell venting, physical changes and escaping electrolyte were made.

The most violent reaction documented involved the explosion of high power lithium-thionyl chloride cells<sup>(40)</sup> when punctured by a nail. Some minor heating (10-20°C) was documented in lithium-copper oxide cells<sup>(50)</sup>.

## SECTION 6

### DISCUSSION

The assessment of hazards associated with the disposition of waste lithium batteries is based upon four factors: 1) the toxicity of cell materials, including those formed as the result of electrochemical reactions or reactions with water or heat; 2) the probability of the material escaping containment; 3) the quantity of toxic material escaping containment; and 4) the personnel safety hazard, i.e., the potential for fire, explosion, or toxic substance release during waste disposal operations. The author's evaluation of these four factors for the various lithium systems is described here.

Perusal of Table 4-3 reveals that five of the lithium battery systems surveyed utilize the following basic components which are classified highly toxic substances<sup>(4)</sup>: 1) thionyl chloride, 2) sulfur dioxide, 3) manganese dioxide, 4) iodine, and 5) vanadium pentoxide. Furthermore, the lithium-polycarbon monofluoride battery produces a toxic compound, lithium fluoride, as the by-product of the electrochemical reaction taking place in the cell. However, of these six compounds, only the thionyl chloride and sulfur dioxide are hazardous by skin contact or inhalation. The other four toxic materials found in the other batteries must either be ingested, injected or placed under the skin to produce toxic effects. This is significant from a (personnel) handling viewpoint, since human ingestion, injection, or subcutaneous application of these toxic materials is not likely to occur during normal collection, processing, or disposal operations. These materials may, therefore, escape containment and still not represent a significant personnel hazard. However, specific precautions must be taken by waste processing personnel when handling either thionyl chloride or sulfur dioxide. These materials may represent a significant personnel hazard if they escape containment.

Lithium-thionyl chloride, lithium-sulfur dioxide, lithium-polycarbon monofluoride, and lithium-vanadium pentoxide systems have basic components which will react with water to produce hazardous substances (Table 4-2). From a personnel safety point of view, the thionyl chloride and sulfur dioxide system require special handling. Thionyl chloride may react violently when it contacts water while sulfur dioxide produces suffocating corrosive fumes. According to toxicity data in Table 4-2, all lithium batteries surveyed in this

study will produce toxic or corrosive gases when heated to decomposition. This suggests that lithium batteries should not be incinerated.

The probability of toxic materials escaping containment as well as a prediction of the quantity of material escaping are basically nonquantifiable parameters. The key issues are 1) whether or not cell cases remain intact, and 2) the number and size of cells which are used and eventually disposed of. The outer cases of lithium cells disposed of using conventional, nonhazardous, waste disposal techniques will eventually corrode, exposing the internal components. Although consistent placements of total lithium battery sales at "less than one percent of total battery sales" were encountered throughout this study, sales figures and distribution patterns were not available. The environment impact of lithium batteries will depend upon the type of cell (toxic chemical involved) and the localized concentration of cells. The lithium from a single cell will probably represent little or no environmental hazard. However, a large number of breached cells releasing their contents to the environment may pose a significant problem. These problems have not been fully studied and addressed. A single relevant study by Crumrine et al<sup>(51)</sup> provides a model which can be used to measure environmental impact of breached lithium cells. However, this model requires the knowledge of the amount and purity of the toxic substance under study. These data were not available from the manufacturers. The Crumrine study addressed the problem of cyanide production in lithium-sulfur dioxide cells. The study concluded that lithium-sulfur dioxide cells be disposed of in sanitary landfills. The study further recommended that large numbers of cells be disposed of at either sanitary or secured landfills which practice leachate monitoring.

An evaluation of personnel safety hazards was performed by 1) examining the behavior of various lithium battery systems under abuse conditions, and 2) reviewing accident data.

The results of abuse tests should provide some indication of inherent safety hazards. During this study, abuse test data were reviewed for this purpose. The review of existing abuse test data yielded the following information:

- 1) External short circuit tests of unfused lithium-sulfur dioxide, lithium-thionyl chloride and lithium-polycarbon monofluoride cells resulted in the activation of vent mechanisms. Gases vented by thionyl chloride and sulfur dioxide

cells may contain hydrogen cyanide, sulfur dioxide or sulfur chloride. Lithium-thionyl chloride cells have also deformed and exploded under external short circuit conditions.

2) Immersion (in fresh or salt water) and drop tests of intact cells at approximately 25°C produced no hazardous situation.

3) Cell deformation (crush) tests resulted in the venting of lithium-sulfur dioxide cells. It is significant that sulfur dioxide gas is irritating and toxic.

4) Foreign object penetration tests caused minor heating (10°-20°C) in lithium-copper oxide cells and explosion in lithium-thionyl chloride cells.

5) Explosions are likely if the internals of lithium cells are allowed to reach the melting point of lithium (approximately 180°C). This is particularly true of those cells which produce elemental sulfur (some lithium-sulfur dioxide chemistries) during discharge.

From this information the conclusion might be drawn that lithium-thionyl chloride, lithium-sulfur dioxide, lithium-carbon monofluoride and lithium-copper oxide cells have significant safety problems. However, the absence of sufficient abuse test data preclude such a conclusion. This information is based on a very small sample of test data and, in the cases of the lithium-carbon monofluoride and lithium-copper oxide, represent the results of one series of abuse tests of one manufacturer's batteries. However, continuing mishaps involving lithium-thionyl chloride and lithium-sulfur dioxide batteries make it difficult to ignore their previous accident histories. The occurrence of at least two accidents<sup>†</sup> (New York and Massachusetts) during the first quarter of 1983 indicates that problems with lithium batteries have not fully been eradicated.

Although verbal accounts were common, little documented evidence exists for accidents occurring in the battery manufacturing and disposal industries. Battery manufacturers either do not keep such records or consider them proprietary information. The only disposal-related accident which could be documented during this survey involved a series of lithium battery fires and explosions occurring at a landfill near Ossining, New York in April 1981. Three dozen drums filled with lithium batteries (not specifically identified but inferred to be thionyl

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<sup>†</sup>Information via personal communications

chloride) caught fire and exploded. These drums had been transported to the landfill for burial. According to the newspaper account<sup>†</sup>, the drums had been left uncovered and in the open for several days prior to the accident. No precipitating cause or explanation was given.

Nondisposal-related accidents involving lithium batteries have been documented for years. Bowers<sup>(20)</sup> and Spencer<sup>(52)</sup> have documented numerous cases of mishaps involving lithium batteries. These studies give indication that lithium-thionyl chloride and lithium-sulfur dioxide batteries are a matter of concern and should be handled with care.

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<sup>†</sup>The Citizen Register, Gannett Newspaper Service, Westchester County, New York, April 21, 1981 edition



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**APPENDIX A**

**GENERALIZED ABUSE TESTS**

TABLE A-1  
MECHANICAL SHOCK TEST (DROP TEST)

Reference(s): 32-38

Cells Tested: Fully charged; partially discharged; overdischarged

Test Temperature: +25°C

Test Description: Free fall of test cell from a height of 5 meters onto concrete test pad

Suggested Evaluation Criteria

<u>Rating</u>	<u>Observation</u>
High hazard	1. Fire/explosion
Moderate hazard	1. Heating of cell (cell wall temperature to 150°C or greater) 2. Venting of toxic, flammable or corrosive gas 3. Leakage of electrolyte
Low hazard	1. Cell breach w/o leakage 2. Change in open circuit voltage 3. Change in weight 4. Venting of nontoxic, nonflammable, noncorrosive gas 5. No change in physical appearance or characteristics other than impact deformation

TABLE A-2  
SHORT CIRCUIT

References: 32,39

Cells Tested: Fully charged; partially discharged; overdischarged

Test Temperature: +25°C

Test Description: 1. Connect terminals of cell through resistance of 0.005 ohms or less  
2. Short circuit for 24 hr

Suggested Evaluation Criteria

<u>Rating</u>	<u>Observation</u>
High hazard	1. Fire/explosion
Moderate hazard	1. Heating (cell wall temperature to 150°C or greater) 2. Venting of toxic, flammable or corrosive gas 3. Leakage of electrolyte
Low hazard	1. Swelling of cell 2. Change in weight 3. Venting of nontoxic, nonflammable noncorrosive gas 4. No change in physical appearance of cell

TABLE A-3  
IMMERSION TEST

References: 33,40

Cells Tested: Fully charged; partially discharged; overdischarged

Test Temperature: +25°C

Test Description: Completely immerse cell for 24 hr in:

- a. Fresh water
- b. Salt water

Suggested Evaluation Criteria

<u>Rating</u>	<u>Observation</u>
High hazard	1. Fire/explosion
Moderate hazard	1. Heating (cell wall temperature to 150°C or greater) 2. Evolution of toxic, flammable or corrosive gas
Low hazard	1. Evolution of nontoxic, nonflammable, noncorrosive gas 2. No reaction



TABLE A-4  
CELL DEFORMATION TEST (CRUSH TEST)

References: 33,52,53

Cells Tested: Fully charged; partially discharged; overdischarged

Test Temperature: +25°C

Test Description:

1. Monitor open circuit voltage of cell and cell wall temperature
2. Crush lower half of cell until internal short circuit develops (noted by a reduction in cell voltage)
3. Maintain compression force for 24 hr

Suggested Evaluation Criteria

<u>Rating</u>	<u>Observation</u>
High hazard	1. Fire/explosion
Moderate hazard	<ol style="list-style-type: none"> <li>1. Heating of cell (cell wall temperature to 150°C or greater)</li> <li>2. Venting of toxic, flammable or corrosive gas</li> <li>3. Leakage of electrolyte</li> </ol>
Low hazard	<ol style="list-style-type: none"> <li>1. Venting of nontoxic, nonflammable, noncorrosive gas</li> <li>2. No leakage or physical change other than impact deformation</li> </ol>

TABLE A-5  
ELEVATED TEMPERATURE TEST

References: 32,43,48

Cells Tested: Fully charged; partially discharged; overdischarged

Test Temperature: 150°C

Test Description: Placed cell or battery in 150°C over for minimum of 24 hr

Suggested Evaluation Criteria

<u>Rating</u>	<u>Observation</u>
High hazard	1. Fire/explosion
Moderate hazard	1. Venting of toxic, flammable or corrosive gas 2. Leakage of electrolyte
Low hazard	1. Venting of nontoxic, nonflammable, noncorrosive gas 2. Swelling of case 3. No change in physical dimensions or weight

TABLE A-6  
INCINERATION TEST

Reference: 49

Cells Tested: Fully charged; partially discharged; overdischarged

Test Temperature: Flame temperatures or furnace heated to at least 540°C

Test Description: Cell or battery exposed to flame environment and incinerated

Suggested Evaluation Criteria

<u>Rating</u>	<u>Observation</u>
High hazard	1. Explosion
Moderate hazard	1. Production of toxic or corrosive gas <sup>*</sup> 2. Increase in flame temperature or observed exothermic reaction
Low hazard	1. Production of toxic or corrosive residue 2. No toxic or corrosive residue after burning

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<sup>\*</sup> Other than those normally associated with the combustion of cellulose products

TABLE A-7  
FOREIGN OBJECT PENETRATION TEST

References: 32,33,43,50

Cells Tested: Fully charged; partially discharged; overdischarged

Test Temperature: +25°C

Test Description:

1. Monitor open circuit voltage and cell wall temperature
2. Penetrate cell with electrically conductive nail, spike or rod - leave in place
3. Monitor open circuit voltage and cell wall temperature for 24 hr

Suggested Evaluation Criteria

<u>Rating</u>	<u>Observation</u>
High hazard	1. Fire/explosion
Moderate hazard	<ol style="list-style-type: none"> <li>1. Heating of cell (cell wall temperature to 150°C or greater)</li> <li>2. Venting of toxic, flammable or corrosive gas</li> <li>3. Leakage of electrolyte</li> </ol>
Low hazard	<ol style="list-style-type: none"> <li>1. Venting of nontoxic, nonflammable, noncorrosive gas</li> <li>2. No leakages or physical change other than impact damage</li> </ol>

# **TECHNICAL REPORT DATA**

*(Please read instructions on the reverse before completing)*

1. REPORT NO.		2.	3. RECIPIENT'S ACCESSION NO.	
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7. AUTHOR(S) B.G. Vincent			8. PERFORMING ORGANIZATION REPORT NO. OH1N6.RG	
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16. ABSTRACT <p>The purpose of the study was to assess the hazards associated with the disposal of waste lithium batteries using existing lithium battery safety test and accident data. A survey was conducted to determine 1) basic cell constituents and electrochemical reaction by-products of the various lithium batteries, and 2) products of reactions between cell constituents and water or heat. An additional survey of solid waste disposal techniques was conducted. This involved the identification of both lithium battery management practices and conventional solid waste disposal techniques. Using the information from these surveys, the hazards associated with the collection, processing, and disposal of waste lithium batteries were quantified. The following conclusions were reached:</p> <p>1) Lithium-thionyl chloride and lithium-sulfur dioxide batteries should be considered potential safety hazards if processed using conventional waste disposal methods.</p> <p>2) Several lithium battery systems, (lithium-sulfur dioxide, lithium-thionyl chloride, lithium-manganese dioxide and lithium vanadium pentoxide) contain highly toxic compounds which may contaminate the environment if released.</p> <p>3) Because of safety and environmental considerations lithium batteries, as a class, should not be incinerated.</p>				
17. KEY WORDS AND DOCUMENT ANALYSIS				
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group
Lithium Batteries Primary Batteries Lithium Battery Safety Waste Management Municipal Solid Waste				
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