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**ENVIRONMENTAL IMPACT ANALYSIS OF ELECTRIC
AND HYBRID VEHICLE BATTERIES**

Final Report

December 16, 1977

Work Performed Under Contract No. EC-77-C-02-4526

**Science Applications, Incorporated
La Jolla, California**

U. S. DEPARTMENT OF ENERGY

Division of Electric Energy Systems

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ENVIRONMENTAL IMPACT ANALYSIS
OF ELECTRIC AND HYBRID
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FINAL REPORT

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December 16, 1977

Prepared for:
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Washington, D.C. 20545

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1. DESCRIPTION OF BATTERY PROGRAM FOR ELECTRIC AND HYBRID VEHICLE APPLICATIONS

1.1 Introduction

The Electric and Hybrid Vehicle Research, Development, and Demonstration Act of 1976 (Public Law 94-413) was enacted on September 17, 1976, by Congressional override of a presidential veto. This Act authorizes the Energy Research and Development Administration, now the Department of Energy (DOE), to establish a Federal Program of Research, Development, and Demonstration to explore electric and hybrid vehicle (and battery) technologies and to demonstrate the commercial feasibility of electric and hybrid vehicles. The major milestones set forth in that Act include:

- September 1977 Characterize current state-of-the-art through vehicle tests.
- December 1977 Promulgate performance standards for vehicles to be purchased or leased for personal and commercial use; report to Congress.
- June 1978 Complete contract for the purchase or lease of up to 2,500 vehicles.
- December 1979 Complete delivery of contracted vehicles (up to 2,500).
- September 1980 Complete revised performance standards.
- March 1981 Complete contract for the purchase or lease of up to 5,000 additional advanced vehicles.
- September 1982 Complete delivery of contracted advanced vehicles (up to 5,000).

The Public Law 94-413 also requires DOE to conduct a continuing assessment of environmental effects and material demands which may result from the electrification of urban vehicles and submit the findings in an annual report to Congress.

The National Environmental Policy Act (NEPA) of 1969 requires that an Environmental Impact Statement be prepared for any federal action which might significantly affect the environment. DOE has established the environmental impact statement schedule in its "Environmental Development Plan for the Electric Vehicle Program:" for meeting NEPA requirements (see Figure 1-1) (1). This environmental impact analysis of electric and hybrid vehicle batteries is one of several studies included in the DOE's environmental impact assessment program. It is intended to identify principal environmental impacts resulting directly or indirectly from the development of electric vehicle batteries. Thus, the result of this study could be used to determine the appropriate following step in the U.S. DOE's EIA process, i.e., negative declaration or Draft Environmental Impact Statement.

The environmental impacts considered in this document are the incremental impacts generated during the various phases in a battery's life cycle. The processes investigated include mining, milling, smelting and refining of metallic materials for electrode components, manufacturing processes of inorganic chemicals and other materials for electrolytes and other hardware components, battery assembly processes, operation and maintenance of batteries, and recycling and disposal of used batteries. The severity of the incremental impacts is quantified to the extent consistent with the state-of-knowledge. It should be noted that many of the industrial processes involve proprietary or patent information, thus in many cases the associated environmental impacts could not be determined.

Fiscal Year

Legend: s - start ○ Indicates either EIS or Negative Declaration.
 c - conclusion (Activity duration not indicated)
 ▲ - milestones

Figure 1-1 Electric Vehicle EIA/EIS Schedule
 Source: Ref. 1.

It should also be pointed out that most candidate battery systems are still in the development phase. Thus, the manufacturing and recycling processes for most battery systems either have not been developed by industry, or the information is not available. For these cases, the associated environmental impact evaluations could only be qualitative and the need for further investigations is indicated.

1.2 Battery Systems for Electric Vehicles

Storage of electrical energy in batteries is a process in which electrical energy is converted to chemical energy during charging and reconverted to direct current electrical energy upon discharge. The most common form of present-day electrochemical storage systems is the lead-acid cell which was originally developed during the 19th century. For general electric vehicle applications, the state-of-the-art lead-acid battery provides rather marginal performance (sixty-mile range at 40 mph). DOE is sponsoring the development of a number of more promising battery concepts which could considerably improve electric vehicle performance. Batteries of potential use in electric vehicles are listed in Table 1-1. These systems, the Zinc-Bromine system and the Lithium-H₂O-Air system are discussed in this report.

It is recognized that the development of improved battery systems with adequate energy capacity, power density and life cycles, and reasonable cost plays an important role in the Electric and Hybrid Vehicle Program. Timing for the near-term and advanced vehicles demonstration project is coupled with the expected availability of improved battery systems. The Federal Battery Research and Development program is primarily carried out by the Argonne and Brookhaven National Laboratories. At the present time, advanced lead-acid, nickel-zinc, nickel-iron and zinc-chlorine battery systems are undergoing concerted development and testing for near-term applications. Sodium-sulfur, lithium-air, iron-air and lithium-metal sulfide batteries are the advanced systems considered for long-range applications. The zinc-air cell listed in References 1, 2 and 3 is not presently being considered by DOE for vehicle applications. Some tables and illustrations from those references have been included in their report without alteration and therefore still include the zinc-air system. In addition to in-house research and development work, the following firms are presently being sponsored by the U.S. DOE to develop specific battery systems for vehicle applications:

Near-term Batteries

Lead-Acid	• ESB, Inc. Yardley, Pennsylvania• C&D Batteries Division of Eltra Corp., Plymouth Meeting, Pennsylvania• Gould, Inc., Rolling Meadows, Illinois• Globe-Union, Inc., Milwaukee, Wisconsin
Nickel-zinc	• Energy Research Corp., Danbury, Connecticut• Yardney Electric Corp., Pawcatuck, Connecticut• Eagle-Picher Industries, Inc., Joplin, Missouri
Nickel-iron	• Gould, Inc. Rolling Meadows, Illinois• Westinghouse Electric Corp., Pittsburgh, Pennsylvania• Eagle-Picher Industries, Inc., Joplin, Missouri
Zinc-chlorine	• Energy Development Associates (owned jointly by Gulf & Western Industries, Inc. and Hooker Chemical Division of Occidental Petroleum Corp.) Madison Heights, Michigan

Advanced Batteries

Lithium-metal sulfide	- Work is managed by Argonne National Laboratory. Key contractors to Argonne are -- • Rockwell International, Atomic International Division, Canoga Park, California• Eagle-Picher Industries, Inc., Joplin, Missouri• Gould, Inc., Rolling Meadows, Illinois• Catalyst Research Corporation, Baltimore, Maryland• Carborundum, Niagara Falls, New York
Sodium-sulfur	• Ford Motor Company, Dearborn, Michigan• Dow Chemical Company, Walnut Creek, California

Iron-air	• Westinghouse Electric Corp., Pittsburgh, Pennsylvania
Lithium-H ₂ O-air	• Lawrence Livermore Laboratory, Livermore, California
	• Lockheed Missiles & Space Company, Palo Alto, California

Table 1-2 summarizes the current research status and DOE's tentative development goals for the candidate battery systems ⁽¹⁾. The specific energy (wh/kg) shown in Tables 1-1 and 1-2 is a measure of the range which these batteries would provide for the electric vehicle. The relative range values ⁽²⁾ for a four-passenger vehicle (commuter car) operated at 40 mph constant velocity when utilizing the various battery systems are listed in Table 1-3.

DOE anticipates that the lead-acid, and possibly the Ni-Zn and Ni-Fe batteries, will be available for the first electric vehicle program demonstration vehicles. All three are expected to be available for the second demonstration. The advanced batteries (zinc-chlorine, sodium-sulfur, lithium-metal sulfide, and metal-air) are planned for the 1980's; however, some of these battery systems may be available for the second electric vehicle demonstration phase.

The allowable proportion of weight for the battery storage system of an electric vehicle is dependent upon the vehicle design. Lightweight construction allows a higher percentage of battery weight. Allowable storage system weight ranges from about 25% to 40% of gross vehicle weight. Reference 3 estimates a 900 to 1400 pound battery weight for a general purpose family car and 600 to 2000 pounds for a commuter car.

In this study, we are concerned only with vehicles that are designed specifically as electric vehicles rather than converted gas-powered vehicles. Design of battery placement

TABLE 1-1
POTENTIAL ELECTRIC VEHICLE BATTERIES

Batteries			Current (October 1975)				Projected			
Systems	Electrolytes	Temp. °C	W-hr/kg	W/kg(peak)	Cycle Life	Cost \$/KWH	W-hr/kg	W/kg(peak)	Cycle Life	Cost \$/KWH
<u>Near-Term (1-2 yr)</u>										
Lead/Acid (SOA)	Aq. H ₂ SO ₄	Room Ambient	30	50	700	50	50	150	> 1000	50
Ni/Fe	Aq. KOH	Room Ambient	44	130	1500	120	60	150	> 1000	120
<u>Intermediate Term (3-5 yr)</u>										
Lead/Acid (Advanced)	Aq. H ₂ SO ₄	Room Ambient	--	--	--	--	50	150	> 1000	60
Ni/Zn	Aq. KOH	Room Ambient	70	110	200	800	90	150	> 1000	50
<u>Long-Term (5 yr)</u>										
(Zn,Fe)/Air	Aq. KOH	Room Ambient	80-120	40	150	2000	90	80	> 1000	60
Zn/Cl ₂	Aq. ZnCl ₂	Room Ambient	66	60	100	2000	130	150	> 1000	50
Li/MS	LiCl-KCl eutectic	400-450	100	120	250	2000	150	300	> 1000	40
Na/S	B-alumina	300-350	90	100	200	2000	170	200	> 1000	40

Source: Reference 2.

Table 1-2 Developmental Goals and Research Status for Batteries

System Description Electrodes Electrolyte Operating Temp.	Battery							
	Lead-Acid	Nickel-Iron	Nickel-Zinc	Iron-Air	Zinc-Air	Zinc-Chlorine	Sodium-Sulfur	Lithium-Metal Sulfide
Electrodes	Lead or lead alloy	NiOON - Fe	NiOON - Zn	Iron-Air	Zinc - Air - Carbon Slurry	Zinc - Chlorine	Liquid-Sodium-Sulfur	Lithium-Metal-Sulfide
Electrolyte	Aqueous H ₂ SO ₄	Aqueous KOH	Aqueous KOH	Aqueous KOH	Aqueous KOH	Aqueous ZnCl ₂	H-alumina	LiCl-KCl eutectic
Operating Temp.	Ambient	Ambient	Ambient	Ambient	Ambient	+10°C	300-350°C	400-450°C
Current State-of-the-Art	In use on 18 Car designs in U.S.	Cell developed by Edison. Have been used in off road applications. Road tested by Westinghouse	Undergoing road tests in Japan, Germany, U.S.	Iron electrode technology is developed but only limited work has been done on an iron-air system	Available for non-vehicle applications	Laboratory tests of electrochemical principles	Laboratory tests	Laboratory tests
Critical Research Needed	Reduction of case, connector, grid weight. Devlop. of corrosion-resistant grid material. Improved high-discharge rate performance	Reduction of expensive nickel utilization. Reduction of self discharge rate (40%/mo.)	Reduction of expensive nickel utilization. Solution to dendrite growth and shape change. Improved high cycle life	Low cost iron electrode. Rechargeable air electrode. Improvement in efficiency.	H ₂ O loss. Electrolyte leakage. CO ₂ contamination. Improved rapid discharge performance	Halogen storage. Control system weight reduction. Solution to dendrite formation	Electrolyte failure. Corrosion caused by sulfur electrode	Sulfur loss. Longer cycle life. Lower cost corrosion-resistant materials
Projected Availability								
Commercialization ^a	Cur. Adv.							
Commercialization ^b	Now 1980 Now 1981-83	1979 1979-80	1979 1980-81	1981 1984	1981 1984	1981 1983-85	1982 1986-90	1982 1986-90
Performance Parameters								
Specific Energy (wh/kg)								
1-3 hr discharge	30 50	40	40-110	80-120	80-120	130	170	113-160
3-7 hr discharge	40 60	60	90-110	NA	90-125	133	NA	NA
Specific Power (w/kg)								
Peak	80-100 130	150-200	150-200	80	30-80	110-130	200-220	150-200
Sustained	30 30	50	50	NA	NA	NA	NA	NA
Energy Efficiency (%)	60-75 60-75	60	60-70	30-40	50	70	60-80	60
Life								
Cycles (deep)	300-800 1000	1500-1000	600-1000	200-100	800	500	1000	1000
Years	7	4	3	NA	NA	5	10	10
Over Cost (\$/kWh)	30-100 30-40	30-110	30-60	25-40	60	50-75	15-40	50-60

^a Approximately 2-4 units^b Greater than approximately 1000 units

Source: Ref. 1

Table 1-3. Relative Range-Miles

	<u>1978</u>	<u>1980</u>	<u>1981</u>
Pb-Acid (Lead-Acid)	60	80	-
Ni-Fe (Nickel-Iron)	70	90	-
Ni-Zn (Nickel-Zinc)	80	110	-
Zn-Cl ₂ (Zinc-Chlorine)	90	-	140
Li-MS (Lithium-Metal Sulfide)	110	-	180
Na-S (Sodium-Sulphur)	-	150	180
Fe, Zn-Air (Metal-Air)	70	-	110
Li-H ₂ O-Air	-	-	-

in an electric vehicle is a function of several factors including vehicle driving response, battery maintenance, battery replacement, and safety. In general, batteries need to be placed low and protected from impact. One concept is a centrally located, strong, and fully enclosed battery-support frame. The safety aspects of this design are good in case of a highway accident.

1.3 Laws, Rules and Regulations Affecting the Battery Program

A number of federal regulatory agencies have jurisdictional authority over actions associated with the production, transport, and use of batteries for electric vehicles. The agencies, that have a dominant role are: The Environmental Protection Agency, the Occupational Safety and Health Administration, and the Department of Transportation.

1.3.1 Battery Manufacture

The EPA has established effluent guidelines and standards for inorganic chemicals, some of which are produced for use in the manufacture of battery systems. A list of these substances and their controls is provided in Table 1-4. The effluent limitations indicate what toxic substances are generally released during the production of materials used in the candidate batteries. There are, at present, no effluent limitations for the production of nickel or lithium. Such limitations would probably be developed if use of batteries containing nickel or lithium significantly increased their production.

The Corps of Engineers has no authority to establish or enforce "no discharge" limitations; however, until EPA has published effluent guidelines which will effectively eliminate the discharge of pollutants into navigable waters, the Corps has compiled recommendations on wastewater effluent which are to be applied to its Urban Studies Program. In the Corps Plan for elimination of the discharge of pollutants by 1985, a list has been compiled of constituents which should be absent from the wastewater

Table 1-4 EPA Effluent Guidelines and Standards

Battery System	Required Substance	Effluent	Effluent Limitations for Production	
			Maximum for any one day	Average of daily values for 30 consecutive days
Lead-Acid	Lead	TSS	50 mg/l	25 mg/l
		Cd	1.0	0.5
		Pb	1.0	0.5
		Zn	10	5
		pH	within the range 6.0 to 9.0	
Lead-Acid	Sulfuric Acid		(Currently under revision)	
Zinc-Bromine	Zinc*	TSS	0.42 kg/kg	0.21
Zinc-Air		As	1.6×10^{-3}	3×10^{-4}
Zinc Chloride		Cd	0.008	0.004
		Se	0.08	0.04
		Zn	0.08	0.04
		pH	within the range 6.0 to 9.0	
Zinc-Bromine	Bromine		"There shall be no discharge of process waste water pollutants... except that residual brine and depleted liquor may be returned to the body of water from which the process brine solution was originally withdrawn."	
Iron-Air	Iron**	TSS	0.0390 kg/kg	.0130
		Cyanide A	.0004	.00013
		Phenol	.0008	.00026
		Ammonia	.0156	.0052
		Sulfide	.0005	.00016
		Fluoride	.0312	.0104
		pH	within the range 6.0 to 9.0	
Sodium-Sulfur	Sodium		(Currently under revision)	
Lithium-Metal sulfide	Aluminum*** (negative electrode)	Fluoride	0.05 kg/kg	0.025
		TSS	.1	.05
		pH	within the range 6.0 to 9.0	

Source: 40 CFR 415 Subparts R, U, and AC revised as of April 1, 1977.
 40 CFR 420.40 revised August 2, 1976.
 40 CFR 421 Subparts B, C, and H.

* Limitations after application of best practicable control technology available.

** Blast furnace method.

*** Standards of performance for new sources.

effluent discharge because of their toxicity to the environment at trace levels. This list includes lead, zinc, cadmium, mercury, and selenium. In addition, other constituents are considered by the Corps to constitute a potential environmental and hygienic risk such that their absence is desirable, although presence at natural background levels may be permissible based upon an environmental scan. These constituents include nickel, antimony, and beryllium. Sodium levels in effluent may need to be limited to less than 10 mg/l, and aluminum to less than 1 mg/l if the characteristics of the region require it. [The COE effluent limitation policy is outlined in 33 CFR 275.]

Standards for ambient levels in water of the metals contained in the candidate battery system are given in Table 1-5.

Within the battery manufacturing plant, restrictions on an employee's exposure to any material required for the battery manufacturing process is enforced by the Occupational Safety and Health Administration. An employee's exposure to these materials in any 8-hour work shift of a 40-hour work week, shall not exceed the 8-hour time weighted average limit given for that material in Table 1-6.

In nearly every case, the OSHA time-weighted average limits correspond to the threshold limit values (TLV's) for chemical substances in the workroom environment established by the American Conference of Governmental Industrial Hygienists. The TLV's are frequently reevaluated, which may account for the few noted discrepancies between published limits on air-borne contaminants of OSHA and those of ACGIH. The chemicals for which there are differences in the published

Table 1-5 EPA Standards and Proposed Criteria for
Ambient Levels of Contaminants in Water

Primary Battery Constituents	EPA National Interim Primary Drinking Water Regulations	Proposed EPA Numerical Criteria for Water Quality (freshwater aquatic life)	Proposed EPA Numerical Criteria for Water Quality (marine water aquatic life)
	Maximum contaminant levels		
Bromine	---	---	---
Iron	---	---	---
Lead	0.05 milligrams/l	30 mg/l	50 mg/l
Lithium	---	---	---
Nickel	---	1/50 LC50	100 mg/l
Sodium	---	---	---
Zinc	---	5/100 LC50	100 mg/l
Secondary Constituents			
Antimony	---	---	---
Beryllium	---	---	---
Cadmium	---	30 mg/l*	10 mg/l
Chloride	---	---	---
Mercury	0.002 milligrams/l	0.2 mg/l	1.0 mg/l
Potassium	---	---	---
Sulfur	---	---	---

*This level is for water with hardness greater than 100 mg/l;
for water with hardness less than 100 mg/l the criteria
would limit the level of cadmium to 4 mg/l.

Table 1-6 Limitations on Air Contaminants in the Workroom

	OSHA		ACGIH			
	<u>Adopted Values</u>		<u>Adopted Values</u>		<u>Tentative Values</u>	
	Time-Weighted Averages		Time-Weighted Averages		Short-Term Exposure Limit	
	<u>ppm</u>	<u>mg/m³</u>	<u>ppm</u>	<u>mg/m³</u>	<u>ppm</u>	<u>mg/m³</u>
Antimony (catalyst)	---	0.5	---	0.5	---	---
Beryllium (by-product)	---	2*	---	0.002	---	0.025
Bromine	0.1	0.7	0.1	0.7	0.3	2
Iron oxide fume	---	10	---	5	---	10
Lead, inorganic, fumes and dust	---	0.2	---	0.15	---	0.45
Lithium hydride	--	0.025	---	0.025	---	---
Nickel	---	1	---	1	---	---
Nickel carbonyl**	0.001	0.007	0.05	0.35	---	---
Selenium (by-product)	---	0.2	---	0.2	---	---
Sodium hydroxide	---	2	---	2	---	---
Sulfuric acid	---	1	---	1	---	---
Zinc oxide fume	---	5	---	5	---	10

* Acceptable ceiling concentration is 5 mg/m³, and accepted maximum peak above acceptable ceiling concentration for an 8-hour shift is 25 mg/m³ for a maximum of 30 minutes.

**Likely to result in recycling of nickel batteries.

value limits are beryllium, iron oxide fume, lead, and nickel carbonyl.

1.3.2 Transportation of Batteries and Battery Materials

Regulations governing the transport of hazardous materials are promulgated by the U.S. Department of Transportation. These regulations specify conditions for transport of most of the primary constituents of the batteries proposed for electric vehicles. The regulations have been developed for the purpose of providing an adequate level of safety for the public under normal conditions, as well as of minimizing the dangers that would result from anticipated accidents.

The responsibility for enforcement of the regulations is divided as follows:

<u>Means of Shipment</u>	<u>Agency</u>
aircraft	Federal Aviation Administration
vessels	U.S. Coast Guard
highway vehicles	Federal Highway Administration
railroad	Federal Railroad Administration
(general authority)	Materials Transport Bureau

The materials Transport Bureau exercises its enforcement responsibility through the Office of Hazardous Materials Operations which may initiate investigations, conduct hearings, and issue orders directing compliance with the regulations.

A list of proposed battery constituents and a summary of the regulations affecting their transport are given in Table 1-7. This table does not include such things as regulations for export, for shipment of small quantities, or manufacturing specifications of cardboard, metal drums, or other packaging materials.

One of the obvious things noted in glancing over the table is that shipment on passenger carrying aircraft or railcars is forbidden for wet batteries and for most of the primary constituents of the advanced battery systems. This should not be a major problem, however, since most batteries are shipped on non-passenger railcars and trucks. The regulations on the shipment of batteries are addressed to conventional lead-acid batteries and would probably be amended with additional precautionary restrictions for the transport of advanced batteries. Furthermore, it can be seen that the regulations for shipping batteries with the auto or auto parts associated with them, are less stringent than the regulations for shipping batteries alone. The shipment of electric vehicles with batteries intact would probably require eventual modification of the regulations reflecting the increased risks due to the greater mass of battery material per vehicle.

Several of the primary constituents of proposed battery systems are not listed among the substances for which there are current shipping regulations. In this category are zinc and nickel.

Table 1-7 DOT Regulations for Packaging and Shipping Hazardous Materials

Substance	Hazard class	Label required	Packaging	Maximum net quantity in one package		Water shipment requirements	49 CFR Sect.
				Passenger carrying aircraft or railcar	Cargo only aircraft		
Battery, dry	(Not subject to Parts 170-169 of this subchapter)						
Battery, electric storage, wet	Corrosive material	Corrosive	Batteries must be completely protected so that short circuits will be prevented. Batteries must be packaged and loaded or braced to prevent damage in transit.	Forbidden	No limit		173.260
Battery, electric storage, wet	Corrosive material	Corrosive	Batteries must be boxed or crated and loaded, blocked or braced in the vehicle to prevent movement during transit. Load must be arranged so that loose articles do not come in contact with batteries, so that short circuits will be prevented, and so that leakage of acid will not occur under conditions normal to transit.	No limit	No limit	Keep dry	173.250
Electrolyte (acid) battery fluid (not over 47% acid)	Corrosive material	Corrosive	If carried in tank cars, they must be lined. May be transported in rubber drums. Complete package with container of electrolyte must be capable of withstanding at least 2 drops from a height of 4 feet onto solid concrete without leakage or rupture of inside containers.	1 quart	5 gallons	Glass carboys in hamper not permitted under deck	173.257
Electrolyte (acid) or alkaline (corrosive) battery fluid packed with dry-storage battery.	Corrosive material	Corrosive	If shipped in glass bottles within a wooden box, bottles may not hold more than 1 gallon, and box may not hold more than 2 gallons. Bottles must be well cushioned and separated from batteries by a solid wooden partition.	Forbidden	5 pints	Carboys in plywood drums not authorized for transport by air.	173.258

Table 1-7 DOT Regulations for Packaging and Shipping Hazardous Materials (Continued)

Substance	Hazard class	Label required	Packaging	Maximum net quantity in one package		Water shipment requirements	49 CFR Sect.
				Passenger carrying aircraft or railroad	Cargo only aircraft		
			If shipped in polyethylene containers inside fiberboard boxes; no more than 12 containers may be put in a box, each container may hold no more than 64 ounces, and the box may weigh no more than 56 pounds.				
Lead dross or scrap	ORM-C (Other regulated material having characteristics which make it unsuitable for shipment unless properly identified and prepared)	None				Segregate same as for corrosive materials. Must be packaged in: (1) steel barrel or drum; (2) wooden barrel or keg; or (3) wooden box	173.1010
Sulfuric acid	Corrosive material	Corrosive	Authorized packagings include: (a) wooden boxes with glass containers, each container holding no more than 1 gallon, or one glass container holding 3 gallons (b) fiberboard boxes with glass containers holding 5 pints each, and not more than 6 containers per box. (c) polystyrene cases with glass containers holding 5 pints each, and not more than 4 containers per box. (d) rubber or phenolic lined drums and tanks for acid concentration of up to 65.25%; shipment in drums or tanks of stainless steel or other corrosion resistant steel for acid concentration higher than 65.25%	1 quart Carboys in boxes, kegs, or drums are not authorized for shipment by air	1 gallon	Keep dry. Under deck stowage is permitted on cargo vessels only in metal drums	173.272

Table 1-7 DOT Regulations for Packaging and Shipping Hazardous Materials (Continued)

<u>Substance</u>	<u>Hazard class</u>	<u>Label required</u>	<u>Packaging</u>	<u>Maximum net quantity in one package</u>		<u>Water shipment requirements</u>	<u>49 CFR Sect.</u>
				<u>Passenger carrying aircraft or railcar</u>	<u>Cargo only aircraft</u>		
Sulfuric acid, spent	Corrosive material	Corrosive	Authorized packagings include: (a) wooden boxes with glass or earthenware containers holding not over a gallon each, or one container holding 1 gallon; (b) tank cars; if product gives off noxious fumes, the tank car must not be vented.	Forbidden Carboys in boxes or plywood drums are not authorized for shipment by air	1 quart	Under deck storage is permitted on cargo vessels only in metal drums	173.248
Bromine	Corrosive material	Corrosive	Authorized packagings include: (a) wooden boxes with glass containers holding up to 1 quart each; or with stone or earthenware jugs not over 1 gallon each. (b) lead-lined metal barrels or drums not over 10 gallons each. (c) tank car with nickel or lead lining; maximum quantity of liquid bromine allowed per tank is 60,000 pounds or 300 percent of the water weight capacity of the tank whichever is less; total quantity loaded must not be less than 98 percent of the quantity the tank is authorized to carry. (A tank constructed and maintained as a Specification DOT-105A500W is authorized for larger capacities of bromine.) Vacant space above the liquid must not be less than 15% of capacity for inside containers or 10% for other containers. Inside containers must have stoppers ground to fit, or threaded caps with bromine resistant	Forbidden	1 quart	Keep cool	173.252

Table 1-7 DOT Regulations for Packaging and Shipping Hazardous Materials (Continued)

<u>Substance</u>	<u>Hazard class</u>	<u>Label required</u>	<u>Packaging</u>	<u>Maximum net quantity in one package</u>		<u>Water shipment requirements</u>	<u>49 CFR Sect.</u>
				<u>Passenger carrying aircraft or railcar</u>	<u>Cargo only aircraft</u>		
			gaskets and elastic material cushioning to insure tight closure. Bottles and jugs must be cushioned with incombustible packaging material which will not produce heat when mixed with bromine. (Hay, saw dust, excelsior, and other organic material is prohibited). Not more than 15 quarts of bromine in bottles nor more than 12 quarts in jugs may be packed in one box. Bromine which has been dried may be shipped in special drums equipped with gaskets of a material approved by the Bureau of Explosives; or in bottles inside fiberboard boxes, but these boxes may not be shipped by air.				
Iron Mass or sponge not properly oxidized	Flammable solid	Flammable solid	Must be packed in hermetically sealed metal-lined wooden boxes or air-tight metal containers.	Forbidden	Forbidden	Separate from flammable gases or liquids, oxidizing materials, or organic peroxides.	173.174
Iron Mass or sponge, spent	Flammable solid	Flammable solid	Must be loaded in open steel cars or open highway vehicles with steel bodies. After exposure to air for not less than 10 days, it may be carried by water in all-steel barges having open holds.	Forbidden	Forbidden	Separate from flammable gases or liquids, oxidizing materials or organic peroxides.	173.174

Table 1-7 DOT Regulations for Packaging and Shipping Hazardous Materials (Continued)

<u>Substance</u>	<u>Hazard class</u>	<u>Label required</u>	<u>Packaging</u>	<u>Maximum net quantity in one package</u>		<u>Water shipment requirements</u>	<u>49 CFR Sect.</u>
				<u>Passenger carrying aircraft or railcar</u>	<u>Cargo only aircraft</u>		
Sodium, metal or metallic	Flammable solid	Flammable solid and Dangerous when wet	Must be packaged in one of the following: (a) air-tight metal packaging inside, wooden boxes (b) metal drums meeting specifications for steel thickness, seams, rolling loops and closure as established for holding sodium. (c) non-sparking air-tight metal container in fiber-board boxes (d) tank cars or tank vehicles having exterior heating coils welded to shell so that material may be loaded in molten form, but material must not be allowed to solidify before being transported. Vacant space above load must be 5 percent or more for sodium at fusion temperature of 208°F.	Forbidden	25 lbs.	Accepted on cargo vessels but forbidden on passenger vessels. Segregation same as for flammable solids labeled Dangerous when wet	173.206
Sulfur	ORM-C	None				Protect from sparks and open flame. Stow separate from oxidizing materials. Segregation same as for flammable solids. Must be packaged in one of the following: (1) metal barrel or drum (2) wooden barrel or keg (3) wooden or fiber-board box (4) sift-proof multi-walled paper bag (5) sift-proof paper-lined burlap bag (6) tight rail car	173.1080

Table 1-7 DOT Regulations for Packaging and Shipping Hazardous Materials (Continued)

<u>Substance</u>	<u>Hazard class</u>	<u>Label required</u>	<u>Packaging</u>	<u>Maximum net quantity in one package</u>		<u>Water shipment requirements</u>	<u>49 CFR Sect.</u>
				<u>Passenger carrying aircraft or railcar</u>	<u>Cargo only aircraft</u>		
Lithium metal	Flammable solid	Flammable solid and dangerous when wet	Must be packaged in one of the of the following: (1) air-tight metal packaging inside wooden boxes (2) metal drums meeting specifications for steel thickness, seams, rolling hoops and closure as established for holding lithium (3) air-tight metal containers inside metal drums, cushioned with incombustible packing material (4) air-tight metal containers individually nested in double-faced corrugated partitions of at least 200-pound test and surrounded by double-walled corrugated liner inside fiberboard boxes.	Forbidden	25 pounds	Segregation same as for flammable solids labeled Dangerous when wet	173.206

One of the important considerations related to the proliferation of advanced battery systems and not yet included in regulations on shipment, is the transport of the batteries that have been discharged and are being recycled. The accident hazards associated with the compounds inside the cases of spent batteries may be somewhat different from those hazards associated with the newly manufactured battery.

The regulations given in Table 1-7 have been established to provide a specific level of safety. Exemptions from complete compliance with the regulations are permitted if other safety measures are taken to ensure the same level of safety. Such exemptions would allow the use of containers or packaging that was not taken into consideration at the time the regulations were developed. (Procedures to obtain such exemptions are given in 49 CFR 107.)

1.3.3 Accidents During Transport

A report must be made to the U.S. Department of Transportation in the event of certain incidents which may occur during the course of transport, loading, unloading and temporary storage and which occur as a direct result of hazardous materials. These incidents include the following:

- (1) a person is killed;
- (2) a person receives injuries requiring hospitalization;
- (3) estimated carrier or other property damage exceeds \$50,000; or
- (4) a situation exists that, in the judgement of the carrier, should be reported (example: a continuing danger to life exists at the scene of the incident).

It is the responsibility of the carrier to make the report at the earliest practicable moment by telephoning the Department of Transportation (202-426-1830). This report must be followed within 15 days by a written report. Any unintentional release of hazardous materials from a package (including a tank) must also be reported in writing within 15 days. (Written reports are sent to the Secretary, Hazardous Materials Regulations Board, Department of Transportation, Washington, D.C. 20590.)

1.3.4 Installation and Use of Batteries in Electric Vehicles

The Society of Automotive Engineers (SAE) has published standards and recommended practices for storage batteries. The standards apply to lead-acid batteries and include standard dimensions, hold-down designs, and terminal posts. Procedures for testing batteries are given, including tests for cold cranking, reserve capacity, overcharge life, and vibration. There is an SAE standard for grounding of storage batteries (SAE J538a) which stipulates:

The negative side of the storage battery shall be securely and adequately grounded so that the voltage drop to the starting motor is held within the limits shown on the following table:

<u>System Voltage</u>	<u>Voltage Drop Per 100 Amps*</u>	<u>Use</u>
6 V	0.12 V	Light with Medium Duty
12 V	0.200 V	Light with Medium Duty
24 V	0.400 V	Light with Medium Duty
12 V	0.12 V	Heavy Duty
24 V-32	0.200 V	Heavy Duty

*Assumes a normal circuit temperature of 68°F.

While there are currently no SAE standards for batteries being used for electric vehicles operated on roads and highways, some of their installation recommendations for storage batteries used in diesel earthmoving equipment may be seen as guidelines. These recommendations (SAE J930a) are as follows:

- (a) easy access for electrolyte level and gravity checks and for water additions;
- (b) adequate ventilation to limit the battery temperature rise in hot climates and to allow escape of evolved gas;
- (c) resonant conditions in a frequency range from 3 to 300 cps should not exist with battery installed;
- (d) battery hold downs and boxes should be made resistant to corrosion by electrolyte;
- (e) hold downs should be designed to distribute force over the wall and/or solid partition areas of the battery case;
- (f) clearance should be provided around uninsulated parts to minimize risk of accidental shorts and excessive self-discharge; and
- (g) flexible leads such as welding cable between battery assemblies and junction blocks will minimize stresses on the terminals.

The SAE Electric Vehicle Technical Committee put together an electric vehicle test procedure (SAE J227) which was published in 1971. These recommended test procedures are intended to provide uniform conditions for reporting vehicle characteristics and include battery tests.

The Federal Highway Administration has promulgated rules governing battery installation which are as follows:

"Every storage battery on every vehicle, unless located in the engine compartment, shall be covered by a fixed part of the motor vehicle or protected by a removable cover or enclosure.

Removable covers or enclosures shall be substantial and shall be securely latched or fastened. The storage battery compartment and adjacent metal parts which might corrode by reason of battery leakage shall be painted or coated with an acid-resisting paint or coating and shall have openings to provide ample battery ventilation and drainage. Wherever the cable to the starting motor passes through a metal compartment, the cable shall be protected against grounding by an acid and waterproof insulating bushing. Wherever a battery and a fuel tank are both placed under the driver's seat, they shall be partitioned from each other, and each compartment shall be provided with an independent cover, ventilation, and drainage".

[49 CFR 393.30]

This regulation probably would be applicable to the installation of lead-acid batteries in electric and hybrid vehicles, but would not provide the same level of safety if advanced battery systems were installed.

In its advance notice of proposed rulemaking on electrical system integrity (Fed. Reg. Vol. 40, No. 172 Sept. 4, 1975 pp. 40853-4), the National Highway Traffic Safety Administration noted "there is sufficient evidence to demonstrate that the electrical system plays an important role in the vulnerability of vehicles to fires" and intended to promulgate requirements for motor vehicle electrical systems. Although one of the primary concerns was that spilled fuel may be ignited, and this would not be an issue in totally battery operated vehicles, the concern remains a valid one for hybrid vehicles. The measures suggested at that time for reducing the risk of fires from battery systems included the following:

- (a) use of nonconductive, impact-resistant battery housing to minimize the likelihood of arcing as an ignition source;

- (b) retention of physical integrity of the battery after impact;
- (c) automatic electric circuit deactivation in severe crashes;
- (d) prescribed voltage operating limits at specified safety component terminals under prescribed conditions of engine speed and accessory load;
- (e) use of redundant and fail-safe components to ameliorate effects of malfunction of components critical to operation of the total vehicle electrical system or major parts thereof;
- (f) battery design which reduces "gassing" and thereby ameliorates the possibility of explosion initiated by sparks during connection or disconnection of battery cables

There are safety requirements for the charging and recharging of storage batteries. These regulations, promulgated by the Occupational Safety and Health Administration [29 CFR 1910.178 (g)], apply to the maintenance of batteries for industrial trucks such as fork lifts, platform lifts and motorized hand trucks. Although these regulations are not meant to apply to the maintenance of batteries for road vehicles, they are listed here because the charging and recharging of batteries for electric vehicles would warrant following these precautions:

- (1) Battery charging installations shall be located in areas designated for that purpose.
- (2) Facilities shall be provided for flushing and neutralizing spilled electrolyte, for fire protection, for protecting charging apparatus from damage by trucks, and for adequate ventilation for dispersal of fumes from gassing batteries.
- (3) When racks are used for support of batteries, they should be made of materials nonconductive to spark generation or be coated or covered to achieve this objective.
- (4) A conveyor, overhead hoist, or equivalent material handling equipment shall be provided for handling batteries.

- (5) Reinstalled batteries shall be properly positioned and secured in the truck.
- (6) A carboy tilter or siphon shall be provided for handling electrolyte.
- (7) When charging batteries, acid shall be poured into water; water shall not be poured into acid.
- (8) Trucks shall be properly positioned and brake applied before attempting to change or charge batteries.
- (9) When charging batteries, the vent caps should be kept in place to avoid electrolyte spray. Care shall be taken to assure that vent caps are functioning. The battery (or compartment) cover(s) shall be open to dissipate heat.
- (10) Smoking shall be prohibited in the charging area.
- (11) Precautions shall be taken to prevent open flames, sparks, or electric arcs in battery charging areas.
- (12) Tools and other metallic objects shall be kept away from the top of uncovered batteries.

As in other existing regulations, the batteries are assumed to be lead-acid ones; different and probably more stringent precautions of a similar nature would have to be developed for the safe charging and recharging of other battery systems.

LITERATURE CITED - SECTION 1

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2. Introduction to the ERDA Electric and Hybrid Vehicle Demonstration Project, Energy Research and Development Agency, Division of Transportation Energy Conservation, Electric and Hybrid Vehicle Research Development and Demonstration Project Office, March 1, 1977.
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2.0 DESCRIPTION OF THE BATTERY INDUSTRY

The existing battery industry relative to electric vehicle application varies from a mature manufacturing industry for the lead-acid battery to research activities for advanced systems such as the sodium-sulfur battery. Correspondingly, the description of the battery industry will be detailed and quantitative for the lead-acid industry and more qualitative for the advanced battery concepts. In addition to the lead-acid battery, the nickel-zinc battery manufacturing process is well defined.

The battery industry description is presented in terms of the battery raw materials, the manufacturing process including materials used and wastes produced, battery recycling, and existing pollution control technology.

2.1 Raw Materials

The raw materials forming an electric vehicle battery include materials for the positive electrode, negative electrode, electrolyte, cell container, terminals and grids and battery casing. Also of interest for the study here are other materials used in the manufacturing process of the battery. The materials for the lead-acid, nickel-zinc, nickel-iron are well defined as these batteries have been manufactured. The long-term advanced battery systems are still in the research and development stage and not all of the material selections are final. For the advanced batteries, the materials identified are based on the currently conceived designs as represented by laboratory test cells and related research work. Table 2-1 summarizes the materials identified for the subject battery systems. The information in the Table was obtained from references 1 through 9 and from communication with the research organizations developing the various battery concepts.

<u>Lead-Acid</u>	<u>Nickel-Iron</u>	<u>Nickel-Zinc</u>	<u>(Zinc, Iron)- Air</u>	<u>Zinc-Chlorine</u>	<u>Lithium-Metal Sulfide</u>	<u>Sodium-Sulfur</u>	<u>Zinc-Bromine</u>
<u>Battery Materials</u>			<u>Zinc Cell</u>				
Lead Oxide	Nickel	Nickel	Mercury	Zinc	Lithium	Sodium	Zinc
Antimony	Iron	Zinc	Zinc	Chlorine Gas	Iron Sulfide	Sulfur	Bromine
Arsenic	Potassium	Potassium	Zinc	Water	{FeS ₂ }	Carbon	Zn Br ₂
Calcium	Hydroxide	Hydroxide	Chloride	Titanium	Stainless	β-alumina	Mn(OH) ₂
Sulfuric Acid	Nickel Oxide	Cobalt	Manganese	Carbon	Steel	{Na ₂ O-Li ₂ O- Al ₂ O ₃ }	Titanium
Water	Copper	Copper	Dioxide	Zinc Oxide	Rigid Plastic	Stainless	Carbon
Casing	Titanium	Titanium	Cadmium	Zinc	Aluminum	Steel	(CH ₃) ₄ NC104
Vulcanized	Rigid Plastic	Nickel Oxide	Lead	Chloride	LiCl-KCl	Glass	Rigid Plastic
Rubber	FeS	Rigid Plastic	Rigid	Rigid Plastic	Boron-Nitride	Rigid Plastic	Ruthenium
Polyethylene	Mercuric Oxide	Hg O	Plastic		Cu ₂ S		Oxide
Nylon	Cadmium Oxide	Nickel Carbonyl	Activated		B ₂ O ₃		Titanium
	Nickel Carbonyl	Chlorine	Carbon		Molybdenum		Oxide
<u>Process Materials</u>		Zinc Oxide	<u>Iron Cell</u>		Beryllia (BeO)		
Water		Lithium	Iron		Yttria (Y ₂ O ₃)		
CaSO ₄		Sodium	Activated		Asbestos Fiber		
Caustic Soda		Hydroxide	Carbon		Niobium Braze		
<u>Manufacturing Wastes</u>					Calcium		
Lead					Li ₂ S		
Lead Oxide							
Sludge							
Lead							
Lead Sulfate							
Lead Hydroxide							
Calcium Sulfate							
Acid Wastewater							
As							
Sb							

Table 2-1. Materials Found in Electric Vehicle Battery Manufacture

Also of interest is the weight composition of the batteries. Table 2-2 presents the weight composition on a per vehicle basis. Many of the materials listed in Table 2-1 could not be quantified. However, in general, the materials that could not be quantified are used in either small quantities or are relatively common material used industrially. Where data was not directly available estimates of materials quantities were made based upon the basic chemical reaction for the battery and the projected achievable energy density.

<u>Lead-Acid</u>		<u>Nickel-Iron*</u>		<u>Nickel-Zinc*</u>		<u>(Zinc, Iron)-Alr</u>	<u>Zinc-Chlorine</u>		<u>Lithium-Metal Sulfide</u>		<u>Sodium-Sulfur</u>		<u>Zinc-Bromine</u>
Lead	440 kg	Iron	59 kg	Nickel	165 kg	Data not available	Zinc	148 kg	Lithium	29 kg	Sodium	30 kg	Data not available
Sulfuric Acid (87% H ₂ SO ₄)	194 kg	Nickel	164 kg	Zinc	120 kg		Chlorine	31 kg	Aluminum	26 kg	Sulfur	30 kg	
Antimony	12 kg	Potassium	61 kg	Cobalt	1.5 kg		Titanium	79 kg	FeS ₂	67.9 kg	β-alumina	36 kg	
Ascorbic	0.8 kg								Separator (Baron Nitride)	5.8 kg	Stainless Steel	115 kg	
Calcium	0.8 kg								LiCl-KCl	76.0 kg			
Rigid Plastic	26 kg								Housing (Stainless Steel)	21.9 kg			
									Current Collector	24.0 kg			
									Molybdenum lead (21 kg)				
									Steel ring				
									Al ₂ O ₃ insulator				
									Baron Nitride Separator				
									Plate Hardware	1.2 kg			
									Feedthrough	8.3 kg			
									Yttria or Beryllia (Yttrium 3.8 kg)				
									Cobalt	6.9 kg			

*Major electrode materials only quantified.

NOTE: All calculated quantities are for a "commuter car" as described in Section 1.2.

Table 2-2. Weight Composition of Batteries Per Vehicle

2.2 Manufacturing

The manufacturing process will be described in detail for the lead-acid battery, nickel-iron and nickel-zinc battery. For the remaining battery systems, the manufacturing will be discussed in more general terms.

2.2.1 Lead-Acid Battery

The manufacture of a lead-acid storage battery consists essentially of casting the electrodes; mixing a lead oxide sulfate paste and applying it to the electrodes; curing the electrodes, electrode activation and assembly, or assembly of elements followed by an electrode activation; then washing, decorating and packaging for shipment. A flow diagram of the major production operations in lead-acid storage battery manufacture is presented in Figure 2-1.

The major production operations involved in lead-acid storage battery production include wet and dry charge processes. In a typical production plant, 80% of the batteries go through the dry charge process while 20% go through the wet charge.

In the dry charge process, the electrode element stacks are placed in a container filled with acid and electrical connections are made for the forming process. This charging operation converts the paste to sponge lead in the negative plate and to lead peroxide in the positive plate. During the process, the sulfuric acid becomes slightly more concentrated, and the time required varies from 4 to 20 hours. After the element has been formed, it is removed from the container, permitted to drain for a very short period, rinsed in fresh water, and placed in an oven (or other apparatus) to dry. The dried elements are assembled to a battery case, and the battery posts are then welded in place and the cover sealed to the case. The completed battery is then sent on to washing, painting, and shipping.

In the wet charge process, the elements are first placed in a battery case, welded together, posts connected to them, and the battery filled with acid. These batteries then undergo the same forming process as the dry batteries. After forming, the acid is dumped (and, generally, recovered), fresh acid added, and the battery boost charged. Fresh acid is added to the dumped dilute acid, and the mixture is used in batteries entering the forming process. The battery is then washed, painted, and shipped.

Wastes from battery production are generally water insoluble, having only minimal migration in a landfill environment. However, solubility varies greatly with small changes in pH, and pH varies in soils, ground waters and necessarily in landfill environments. For this reason, those wastes containing heavy metals in any form or concentration have been considered potentially hazardous, due to the possibility of leaching into surface or ground water.

Based on 1973 figures, approximately 700,000 kkg of lead is used in the manufacturing of batteries which represents 50 percent of the total U.S. consumption. Of the total lead produced, 7 percent is lost as waste. Land-destined wastes from the storage battery industry consist largely of sludges from water effluent treatment, the greatest amount of which stems from lead-acid waste water sludges, along with a much lesser amount of rejected and scrap batteries.

Studies done in 1973 on the storage battery industry indicated a disposal of 47.3 kkg of potentially hazardous constituents on land in a total waste stream of 9,235 kkg, consisting of water effluent treatment sludges and rejected and scrap cells. Projections for 1977 and 1983 of land disposed and total stream wastes are as follows:

1977 Land disposal - 467 kkg
 Total waste stream - 162,800 kkg

1983 Land disposal - 625 kkg

Total waste stream - 207,700 kkg

The process waterborne raw wastes consist mainly of suspended and dissolved lead and lead compounds (lead sulfate, lead hydroxide), sulfuric acid and oil and grease in the wash water streams. The possible sources of waste water include:

- Pastemixing and pasting area washdown
- Acid mixing area washdown
- Contact cooling water use after acid filling or during formation
- Oxide production area wet scrubbers
- Oxide production area washdown
- Battery rinse after acid fill or dump
- Dry charge plate wash
- Dry charge formation area washdown
- Final battery wash
- Production area wash
- Wet scrubbers for dust control.

Solid wastes are generated consisting of lead dross, scrap lead, scrap plates, baghouse dust, separators and container scrap. Sump mud, comprised of suspended lead and lead compounds is a raw waste sludge which is settled and collected in sumps or clarifiers. This sump mud may be collected and recycled to the paste mixer or collected and shipped to the smelter for credit.

In addition, the pH of the raw waste stream is found to range from 1 to 7.

The wastes from lead-acid battery production include the following:

- Wastes produced from the manufacture of grid materials -- these will include dusts, dross, and rejects of the raw materials and alloys used. This waste amounts to 30 kg per 1000 kg of product and is comprised of lead and lead alloys.

- Wastes produced from the cathode and anode paste preparations. This waste amounts to about 2 kg per 1000 kg of product as lead and lead oxide paste.
- Wastes produced from clean-up of the pasting area. This amounts to 5 kg per 1000 kg of product in the form of lead oxide and lead powders suspended in a water effluent of about 750 kg of water.
- Wastes produced from reject plates in the curing cycle. These wastes generally consist of 10 kg of lead monoxide and 20 kg of lead per 1000 kg of product.
- Wastes produced from reject assembled elements. These rejects consist of 10 kg of lead monoxide and 20 kg of lead per 1000 kg of product.
- Wastewater solutions. There are water-borne raw wastes comprised of sulfuric acid (typically 2 to 4%) in water containing suspended and dissolved lead. The sources of lead containing wastewater include the pasting area, the dry and wet charge forming areas, and the assembled battery washing area. Also in cases where a battery breaker is located on site with the battery plant, there will be an additional wastewater stream. A typical plant producing 20% wet charge and 80% dry charge batteries would have a lead raw waste factor of 0.331 kg of lead (suspended and dissolved) per 1000 kg of batteries.
- Sludges recovered from treatment of wastewater streams. These wastes consist of lead hydroxide and lead sulfate at 0.541 kg per 1000 kg of product (80% solids basis) for those plants using sodium hydroxide neutralization. The composition of the sludge typically will include lead sulfate (0.293 kg per 1000 kg), lead hydroxide (0.140 kg per 1000 kg) with a water content ranging from 20 to 65%. For those plants using lime neutralization, a calcium sulfate sludge is produced of 735 kg (dry basis) per 1000 kg of product. The composition of the sludge typically will include calcium sulfate (2101 kg per 1000 kg at 35% solids basis), lead hydroxide (0.140 kg per 1000 kg), lead sulfate (0.293 kg per 1000 kg) with a lead content of approximately 150 mg per liter.

Table 2-3 summarizes the wastes resulting from a typical lead-acid battery manufacturing process. The assumptions used to construct the typical plant are:

- 1000 kg of batteries (dry weight) as the production basis;
- 14.99 kg of lead contained in a typical battery;
- 70 gallons (265 liters) of water used to produce one dry charge battery;
- 20 gallons (75.5 liters) of water used to produce one wet charge battery; and
- that the plant process wastewater stream to the treating step contains 4% sulfuric acid and 50 mg per liter of lead.

The resulting treated effluent pollutants in the water discharged are typically:

	<u>mg/l</u>	<u>lb/1000 lb Product</u>
TSS	6.6	0.014
Lead	0.7	0.003
Oil and Grease	7.0	0.016

Table 2-3. Lead-Acid Typical Plant

A. Annual Production	= 8,233,300 kg (dry basis) of batteries
Dry Charge Type	= 6,586,630 kg
Wet Charge Type	= 1,646,670 kg
B. Waste Characterization	
1. Wastewater Treatment Sludge Using Caustic Soda Neutralization	
Pb raw waste factor	= 0.331 kg per 1000 kg batteries
Pb effluent factor	= 0.01 kg per 1000 kg batteries
Pb sludge factor	= 0.324 kg per 1000 kg batteries
Composition of sludge	
PbSO ₄	= 0.293 kg per 1000 kg batteries
Pb(OH) ₂	= 0.140 kg per 1000 kg batteries
Water	= 20 to 65%
80% solids total sludge	= 0.541 kg per 1000 kg batteries
	= 4456 kg per year
OR	
2. Wastewater Treatment Sludge Using Lime Neutralization*	
CaSO ₄ factor	= 735 kg (dry basis) per 1000 kg batteries
	= 2101 kg sludge basis (35% solids) per 1000 kg batteries
	= 17,298,163 kg per year
	= 17,298 metric tons per year
Sludge Characterization	
CaSO ₄	= 2101 kg per 1000 kg batteries
Pb(OH) ₂	= 0.140 kg per 1000 kg batteries
PbSO ₄	= 0.293 kg per 1000 kg batteries
Pb	= 150 mg per liter

* Approximately 20% of the plants in the U.S. use this treatment.

Source: Reference 1.

2.2.2 Nickel-Zinc Battery

Two processes can be used to manufacture the nickel electrode for the nickel/zinc battery. One is the manufacture of thick porous sintered electrodes. The other process is a chemical process forming a bonded nickel electrode.

The basic processes in the manufacture of a sintered nickel electrode are shown in Figure 2-2 in the form of a flow chart. Two specific operations are involved - one with the manufacture of a porous sintered nickel substrate and the other with the impregnation of the nickel substrate with active mass (nickel hydroxide and additive) formed directly in the pores of the substrate from a nickel solution that can be readily prepared from raw materials by simple economical techniques. In this process the physical properties of the substrate (pore size and distribution, porosity, nickel powder content, strength) can be controlled, and porous substrates can be tailored to a particular requirement.

The process for preparation of a partially active positive electrode material for combination into a bonded electrode is a chemical oxidation of a divalent nickel salt, with appropriate control to produce a material of the proper degree of crystallinity and activity level, followed by appropriate recovery measures. Bonding is done with inclusion of a conductive diluent and binder and is then rolled with a proper grid in a continuous process with the rolls of material cut and magazined.

The physical properties of the nickel hydroxide, conductive material (e.g., cobalt or similar metals), and the binder can significantly influence the bonded electrode characteristics, and that at least two of these products (nickel hydroxide and the capacity stabilizer additive) must be manufactured under special conditions to meet the specifications.

Source: Reference 2.

Figure 2-2. Flow Diagram of Manufacturing Process for Nickel-Zinc Batteries

The manufacture of nickel hydroxide, for instance, can be quite complex, and can involve many process steps, some of which are given below:

- Preparation of nickel salt from raw materials (this step is common to both types of electrodes)
- Preparation of the nickel solution at the desired density, acidity, and temperature
- Precipitation of Ni(OH)_2 (e.g., reacting the nickel solution with caustic)
- Filtration of the precipitated Ni(OH)_2
- Washing free of caustic solution
- Drying of the Ni(OH)_2
- Grinding of the Ni(OH)_2
- Sizing of the Ni(OH)_2

Although it is possible to co-precipitate the capacity stabilizer additive at the same time as the Ni(OH)_2 , it is uncertain that the best product would be produced. Consequently, it may require the additive to be produced separately by similar steps as described above. In either case, additional steps over and above those for the manufacture of these two ingredients are required and may include the following:

- Blending of Ni(OH)_2 , additive, and binder in precise amounts
- Possible pelletizing, grinding, and sizing.

The production of finished bonded electrodes is achieved by compacting this active material mixture onto a grid.

Although sintered electrodes offer some benefits over non-sintered electrodes, the processes which are used in sintering could pose environmental difficulties. In the

electrochemical impregnation processes, the final stages include drying. The drying stage could produce airborne pollutants from the electrode material and needs to be studied further.

The processes in the manufacture of zinc electrodes are shown in the flow diagram. There are two basic operations: 1) the preparation of the zinc mass and, 2) the compaction of this mass onto a grid. The specific details in the preparation of the zinc mass may vary somewhat, depending on the form and proportion of the materials used. The steps in the manufacture of the grid are essentially identical to those for the nickel electrode, with the possible exception of the design of the grid. The compaction of the zinc mass can be accomplished by a variety of approaches. The specific manufacturing techniques used depend largely on the electrode configuration desired. Generally, the compaction can be performed using conventional equipment. In volume production, the operations of molding and pressing are envisioned at the present as being done by conventional high-speed presses adapted for this use. The single electrode operation offers greater electrode design flexibility. These compaction steps would be automated to the point necessary for high-volume and low-cost production.

The assembly of the nickel-zinc cell poses no greater obstacles than other volume production batteries such as the automotive lead-acid type. Highly automated assembly lines are possible for the nickel-zinc product. However, for technical reasons, a proper balance in the degree of automation will be necessary in the early years of production.

The selected electrode configuration, separator system, cell design, and hardware design will influence the assembly processes. While certain assembly processes cannot be well

defined at present or are in the conceptual stage, it can be stated that many process approaches are derived from knowledge of the manufacture of batteries in large volume (e.g., automotive and industrial lead-acid batteries).

An integral part of the manufacturing process will be the recycling of waste processing solutions as shown in Figure 2-3. Nickel solids will be recovered and water recycled. However, there will still be an effluent stream from the plant containing nickel solution and solids and caustic solution. Yardney ⁽¹⁰⁾ indicates that approximately 130 gallons of process water will be used per battery produced. The effluent will be treated by neutralizing the alkaline waste water with sulfuric acid. Settling tanks and filters will be used to recover nickel and cobalt solids. The resulting sludge will be sent to reclaimers. Production concepts presently under consideration suggest there will be very little unreclaimed waste in nickel-zinc battery manufacture. Plant designs are largely closed systems.

Source: Reference 2.

Figure 2-3. Recycling of Processing Solutions in Manufacture of Nickel-Zinc Battery

2.2.3 Nickel-Iron Manufacturing Process

The active materials for nickel-iron tubular type cells consist of nickel hydroxide in alternate layers and nickel flake for the positive electrode, and an extremely pure iron- Fe_3O_4 mixture for the negative. The purity and physical nature of the active materials have an extremely important and direct effect on the electrochemical capacity and life cycle characteristics of the system. The various procedures described below are based on the manufacturing information in Reference 9.

"Tubular" nickel hydroxide is made by spraying a nickel sulfate solution into hot sodium hydroxide.¹ The resulting precipitate is filtered, dried, washed, and classified, and, finally, crushed and screened to size as shown in the flow chart (Figure 2-4) and detailed below.

1. Raw material used in the preparation of nickel(II) hydroxide is steam-shattered nickel shot or nickel powder of high purity. Other forms of nickel available to the manufacturers may also be utilized, such as nickel active material from returned cells, or nickel hydroxide and nickel flake fines which are too small in size to be used in tubes.

2. The preparation of the nickel sulfate solution varies somewhat with the raw material being processed. In one procedure, nickel shot is dissolved in 20% sulfuric acid at 100°C (the hydrogen evolved during the reaction is recovered for use in the active iron process), and the solution is adjusted to pH 3-4 by the addition of nickel hydroxide or some other material. After this neutralization the solution is filtered to remove ferrous iron. When other starting materials are used, special purifications to remove copper and other elements are required.

Source: Reference 9.

Figure 2-4. Flow Chart for Processing of Tubular Nickel Hydroxide

3. The nickel sulfate solution is sprayed into a boiling solution of 25-30% sodium hydroxide and the resultant slurry is filtered. The filtrate is treated in a thickener and refiltered to recover fines.

4. The filter cake is dried, washed with hot water to remove sodium hydroxide, carbonates, and sulfates; classified, crushed, and screened.

The negative active material is prepared from pure iron by a process in which iron slugs are dissolved, recrystallized, roasted, reduced, and then partially reoxidized. These steps further purify the material, produce a material which is a stable oxide of good conductivity, and produce a fine powder of high surface area. A typical procedure for this process is shown in the flow chart (Figure 2-5) and detailed below.

1. Iron is dissolved in 20-25% sulfuric acid to form a ferrous sulfate solution. At the same time, hydrogen is evolved and collected for use later in the process.

2. The ferrous sulfate solution, sp. gr. 1.38 - 1.40, is filtered, recrystallized, and dried. The filtration removes any scum or sludge which forms from insoluble impurities in the iron raw material. Crystallization is carried out in open troughs which are water-jacked for cooling. The residual mother liquor is separated from the ferrous sulfate crystals by centrifuging in a lead-lined centrifuge. The mother liquor (after fortification with sulfuric acid) is reused to dissolve raw iron slugs (as in step 1).

The ferrous sulfate heptahydrate crystals, are dried in rotary drum dryers to a monohydrate. This is done at an average temperature of 100°C.

Source: Reference 9.

Figure 2-5. Flow Chart for Processing of Iron Active Material

3. The dried ferrous sulfate is roasted at temperatures between 815°C , in a retort, to ferric oxide. During roasting the material is turned continually by mechanical means, or by periodically hand raking so that uniform decomposition takes place. The gaseous oxides of sulfur, SO_2 and SO_3 , which are given off during the roasting process, are absorbed in an acid absorption tower, and the resulting sulfuric acid is used in step 1 to dissolve the raw iron slugs.

4. The red iron, Fe_2O_3 , is reduced to metallic iron. This reduction is carried out in cast steel pots at temperatures of 650 - 675°C . Hydrogen evolved in step 1 is utilized in this operation, but additional sources, such as a hydrogen cracking generator, may also be used. Reduction by this procedure takes about 12 hours, and requires an additional 6 hours of cooling under a hydrogen atmosphere.

5. The cooled, finely divided Fe material is flooded with hot water before the pots are opened to the atmosphere. This prevents air oxidation of the Fe to undesirable non-conducting oxide forms, such as Fe_2O_3 . Then the damp material is spread out on steam tables and heated to convert the material into a mixture of αFe and Fe_3O_4 .

6. The dried material is ground and screened. Material coarser than 60 mesh is generally returned to the grinder.

The reduction iron material produced in step 4 above is well cooled to an amorphous powder and is micropulverized in a CO_2 atmosphere. This material is known as "Ferrum Reductum", and it is indicative of the high purity of the battery grade material.

Some manufacturers prefer to add a small amount of sulfur as FeS , or mercury as mercuric oxide, to the iron active material; others include cadmium as cadmium oxide. These additives and others which are generally dry-blended are used to increase the life by acting as depassivating agents, increase the conductivity, or reduce the gas evolution on standing in electrolyte by increasing the over-voltage.

Throughout the process the products are subjected to heating, drying, and water and chemical rinsing. Each of the separate phases of the process produces by-products which are possible effluents in the total waste stream. Some of the by-products are captured and reused, such as the sulfuric acid absorbed during the roasting process.

While the total waste stream for the nickel-iron was not quantified, it is plausible that it would parallel that of the manufacture of nickel-zinc batteries.

2.2.4 Advanced Batteries

Manufacturing processes for the advanced battery systems are not defined at this point in their development. Although lithium batteries are currently manufactured, these batteries are made for a totally different application than electric vehicle propulsion and the resulting manufacturing for automatic applications is expected to be considerably different. An experimental Lithium-Water-Air system, designed for automotive use, is currently in the experimental phase. Details of the established lithium battery manufacturing process are presented with the idea in mind that at least the lithium handling procedures may be similar to future processes. The Lithium-Water-Air system is described conceptually. Unfortunately, the developers (Lockheed Palo Alto Research Laboratory) were unable to supply data suitable to estimate environmental impacts should this system become commercially available.

2.2.5 Lithium Cell

The major raw materials used in the lithium cell process are lithium metal, carbon, acetonitrile, sulfur dioxide, asbestos, Teflon, ethyl alcohol and steel. Asbestos was used as a separator in early lithium batteries. However, it is not currently used in preassembly of nickel plated steel cans, preparation of the cathode and anode, cell assembly, testing and packing. The cathode is prepared by proportioning and mixing graphite, carbon, Teflon, ethyl alcohol and water. The wet mixture is mechanically dewatered to achieve a certain moisture content. The mix is then applied to an expanded nickel screen and dried. The cathode material is trimmed to size and leads are attached. The cathodes are then dried overnight in a vacuum oven.

Cell assembly begins with spacing the lithium foil anode around the cathode in a moisture free atmosphere. The cell top is then added and crimped. The electrolyte of sulfur dioxide and

Source: Reference 13

Figure 2-6. Simplified Diagram of Major Operations in Lithium Battery Manufacture

acetonitrile is added to the cell through a small hole in the can. The batteries are dipped and rinsed with an organic solvent, weighed to determine the amount of electrolyte and the hole in the can is sealed. The batteries are stored and aged before testing.

A flow diagram for existing lithium battery production is shown in Figure 2-6.

2.2.6 Lithium-Water-Air Battery

Development of a Lithium-Water-Air Battery for automotive propulsion is currently at the experimental phase. Studies at Lockheed Palo Alto Research Laboratory (LPARL) and Lawrence Livermore Laboratory have examined the feasibility of the concept (report by Bauman and Adams on Energy Conservation for the Department of Energy, 1977). The results of these studies indicate the use of a high-energy density metal or primary system such as the Li-Water-Air Battery is promising as a technically and economically feasible approach to the development of a full performance electric vehicle.

The Lithium-Water-Air Battery and other reactive metal high-power primary batteries compare closely with internal combustion engines thermo-dynamically, and offer the potential of providing an electric vehicle with performance features similar to present-day compact automobiles. Unlike conventional battery designs which require overnight recharging between long trips, the Lithium-Water-Air Battery is recharged by mechanically replacing the active electrodes. In principle, automobiles powered by such batteries would be able to travel hundreds or thousands of miles with only short-duration replenishment stops, analogous to stopping at a service station for fuel.

The system concept involves the periodic replacement of the lithium anode and removal of Li_2CO_3 precipitated during battery

discharge. This would be done at local auto service stations. Carbon dioxide would also be added to the battery as a precipitating agent for lithium ion. The Li_2CO_3 slurry would then be transported to lithium processing plants where it would be reprocessed into lithium metal for anodes.

To date, only test cells have been constructed to investigate the technology involved in the operation of the Lithium-Water-Air Battery. These Lithium-Water cells consist of a lithium anode, an air cathode, and flowing electrolyte. The anode and cathode are maintained in direct contact during discharge. The circulating electrolyte removes heat from the system and allows the maintenance of constant composition by dilution or precipitation techniques. Power varies as a function of electrolyte flow rate, electrode spacing and electrolyte molarity. A five-cell battery was built and tested and was found capable of delivering in excess of 250 watts.

Alternate lithium recovery routes were investigated and methods with greatly reduced energy consumption have been identified. Reprocessing of the lithium salt is basically a two-step process: 1) preliminary winning of the low-lithium content concentrate product in an aqueous electrolyte cell, 2) conversion to pure lithium metal in a fused-salt or liquid ammonia cell. A preliminary cost estimate of 65 cents per pound was developed based on a 50,000 ton per year reprocessing plant. Such a plant could serve an estimated 3 million automobiles.

The original concept of Lithium-Water-Air Battery powered automobiles appears, at least from these preliminary studies, to be technically and economically feasible. Some of the remaining technical issues include:

1. Maximizing the efficiency of anode utilization under varying loads during long duration,
2. The production of inexpensive cathodes with low polarization and long life,

3. Problems inherent in parallel manifolding of cells in a flowing electrolyte,
4. Construction and testing of multi kilowatt modules with design features allowing for rapid and simple anode replacement,
5. Minimization of cost by using non-metallic construction materials.

2.2.7 Carbon-Zinc-Air Cell

The manufacturing process for production of existing carbon-zinc air cells consists of constructing carbon and zinc electrodes, insertion of electrolyte (for pasted cells only) and assembly. The flow diagram for manufacture is shown in Figure 2-7.

Charcoal powder, graphite powder, manganese dioxide and water are mixed. The resultant moist mix is molded into rods. The rods are then dried and cured under controlled temperature and humidity for one week and are then ready for use as positive electrodes. Zinc metal and a small amount of mercury are amalgamated in a pot and molded to form plates which serve as negative electrodes in the battery.

In the water-activated cell process, lime chips and caustic potash are packaged and placed on the bottom of the cell container. The porous activated carbon positive electrode is then inserted and amalgamated zinc plates are positioned on both sides of the carbon electrode. Terminals are then welded on the electrodes and the cell is covered. The zinc electrode is sealed with pitch and the battery is ready for testing, packaging and shipping.

In the pasted cell manufacturing line, zinc electrodes and a carbon electrode are placed in the battery case in the

Figure 2-7. Major Production Operations in Pasted Carbon Air Cell Battery Manufacture

same manner as water activated cells. The space between zinc and carbon is then filled with a gel mix which consists of ammonium chloride, zinc chloride, mercury bichloride, caustic potash, thickener and water. The cell is set aside to allow the gel mix to set, which occurs in about ten to fifteen minutes. The terminals and covers are put in place and the zinc electrodes are sealed with pitch. The application of terminals, cover, and sealing of zinc electrodes by pitch is then accomplished.

The only waterborne wastes from the process come from cleaning of tools. The principal uses of water in the process are for mixing of the carbon electrode for both cell types, for the gel mix of the pasted cells, and for washing of tools. The water used in the mixes is consumed in the product and the wash water is discharged. The details are:

	gal/ton of product
consumed in product	24
wash	12

2.3 Recycling and Disposal of Batteries and Electrolytes

Ideally, all batteries manufactured would be returned for recycling. In practice, approximately 90% of the batteries are returned to the manufacturer for recycling. The existing process for recycling lead-acid batteries is described as well as purpose and procedure for the nickel-zinc battery. In all advanced battery systems recycling procedures will be designed as an integral part of the manufacturing process. It should be recognized that although recycling is a part of all battery manufacturing processes, not all batteries will be returned.

2.3.1 Lead-Acid

Currently, used lead-acid automotive batteries are collected by distributors and returned to the manufacturer. The batteries are broken apart by crushing. The grids, plates, and other lead parts are salvaged and returned to the smelter. The separators and casings are discarded. The electrolyte is processed to remove lead and lead components by neutralization, settling and filtration. If the battery crusher is located at the manufacturing site, the electrolyte is added to normal process wastewater streams where it is eventually treated.

2.3.2 Nickel-Zinc

A major process would involve the recovery of the nickel solids to produce the nickel solution used in the manufacture of the nickel electrode. An alternative, which may also be possible, is the recycling of electrodes whole after a simple cleaning operation. This might be made possible because of the sintered type electrode. The economics of recycling the electrodes whole versus the production of the nickel solution must be weighed carefully, however, in view of the higher initial cost of a longer cycle life electrode and its impact on the cost increase of the

Source. Reference 2.

Figure 2-8. Recycling Schemes for Nickel-Zinc Batteries

battery. These two recycling processes are shown in Figure 2-8.

Appropriate processing schemes could presumably also be worked out for the separate recovery of the zinc mass. Likewise, it is conceivable that the plastic materials (case and cover) could be recycled. Metallic components other than the nickel grids and tabs, namely, terminals, cell and battery connectors, and battery module packaging hardware could be salvaged.

2.4 Existing Pollution Control Technology

Existing pollution control technology for the battery industry consists mainly of treating the wastewater streams from the manufacturing plants and using scrubbers to control fumes and particles in the air. The wastewater is treated to remove the heavy metals and compounds and to neutralize the wastewater. Solid waste scraps are also generated and are replaced in the plant or sold for reclaim. The pollution control procedures for the lead-acid battery manufacture and nickel-zinc battery manufacture are more fully described below.

2.4.1 Lead-Acid

Process wastewater streams in lead-acid battery plants come from acid fume scrubbers, wet dust control scrubbers, posting area washdown (this is sometimes recycled), contact cooling water, dry charge plate wash, battery rinse and wash, production area washdown and miscellaneous acid leaks and spills. Non-process water streams include non-contact cooling water, cooling tower blowout, boiler blowdown and sanitation. In many plants process and non-process water streams are combined before treatment.

There are two general categories of wastewater treatment practiced in existing lead-acid plants. The first type is an in-process control, whereby the water used for washdown of the posting area is collected, treated to remove lead oxide suspended solids by using hydrocyclones and filtering, and recycled for paste area washdown. This technique reduces, but does not eliminate, both the quantity of wastewater generated, as well as the amount of lead in the waterborne raw waste streams. The resultant lead oxide sludge is either re-used for paste mixing, or sold for reclaim.

The second general type of wastewater treatment involves collection of raw waste streams and end-of-pipe treatment.

All plants treat process wastewater by settling in basins, sumps, or pits, to remove and recover lead oxide suspended solids. Most plants use chemical precipitation for removal of metals, clarifiers, or thickeners. The waste water is typically treated with caustic soda, lime, or soda ash, to adjust the water pH.

2.4.2 Nickel-Zinc

Yardney, Gould and Eagle-Picher have proposed manufacturing designs to ANL for nickel-zinc batteries. References 10, 11 and 12 indicate that the pollution control technology will be very similar to that for lead-acid battery manufacture. All process wastewater will be collected, sent to settling tanks, filtered and treated to neutral pH. The sludge collected will be sent to reclaimers. An air scrubber is used to control the fumes from the reaction tank for making the nickel salt solution.

2.4.3 Advanced Batteries

Much of the existing pollution control technology will be applicable to advanced battery manufacturing. Wastewater streams will be neutralized, and settling tanks and filters used to reclaim the metals in the process water. Scrubbers will be used to control fumes and metal particles and compounds in the air. Additional pollution control technology may be required for some of the advanced battery systems.

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3.0 ENVIRONMENTAL IMPACTS OF THE BATTERY PROGRAM

3.1 Incremental Demands Placed on the Industry by the Program

In this section, the incremental demands placed on the battery industry for the Phase I and Phase II portions of the Vehicle demonstration program as well as longer term demands will be described. The incremental demands of concern are increased material needs of the industry, control of increased wastes produced and of new types of wastes, and control of wastes produced by worn out batteries.

3.1.1 Raw Material Demands

The increased raw material demands are summarized in Table 3-1 for the different battery systems. These values were derived using the data in Table 2-2 for material usage per vehicle and scaled to 2500 vehicles for Phase I and 5000 vehicles for Phase II. For long term application it is assumed that a fleet of 10 million electric vehicles exists and that 1 million vehicles are produced annually.

Previous studies have addressed the resource availability problem for full scale electric vehicle application. Table 3.2 is reproduced from Reference 1, and indicates material usage as a percent of 1974 reserves and of identified resources. As can be seen, 10 million electric cars would require a major fraction of U.S. reserves for lithium, antimony, and yttrium. The nickel-zinc battery fleet, however, is well within the constraints of U.S. resources.

The resources and reserves in Table 3-2 should not be considered as firm limitations on feasible use of electric cars. As demand and prices rise, increased exploration and improved methods of recovery will bring forth additional reserves and resources. Furthermore, batteries themselves continue to evolve and each advance leads to a decrease in active materials.

Table 3-1. Material Demands by Phase for Battery Systems (10^6 kg)

Long Term Application	Lead/Acid		Nickel/Iron		Nickel/Zinc		(Zinc, Iron)/Air		Zinc/Chlorine		Lithium/Metal Sulfide		Sodium/Sulfur		Zinc/Bromine	
Long Term Application	Lead	4440	Iron	540	Zinc	1200			Zinc	1480	Lithium	290	Sodium	360		
	Sulfuric Acid	1940	Nickel	1240	Nickel	1650			Chlorine	310	Aluminum	260	Sulfur	300		
	Antimony	120	Potassium	410	Cobalt	15			Titanium	790	FeS ₂	480	8-alumina	160		
	Arsenic	8									BN	60				
	Calcium	8									LiCl-KCl	760				
	Plastic	260									Molybdenum	210				
											Yttrium	38				
Phase I											Cobalt	69				
	Lead	1.1	Iron	0.15	Zinc	0.4			Zinc	0.4	Lithium	0.07	Sodium	0.0075		
	Sulfuric Acid	0.89	Nickel	0.1	Nickel	0.3			Chlorine	0.08	Aluminum	0.065	Sulfur	0.0075		
	Antimony	0.03	Potassium	0.1	Cobalt	0.004			Titanium	0.2	FeS ₂	0.12	8-alumina	0.09		
	Arsenic	0.002									BN	0.015				
	Calcium	0.002									LiCl-KCl	0.19				
	Plastic	0.065									Molybdenum	0.005				
Phase II											Yttrium	0.0095				
											Cobalt	0.017				
	Lead	2.2	Iron	0.3	Zinc	0.8			Zinc	0.8	Lithium	0.14	Sodium	0.15		
	Sulfuric Acid	0.97	Nickel	0.6	Nickel	0.6			Chlorine	0.16	Aluminum	0.13	Sulfur	0.15		
	Antimony	0.06	Potassium	0.2	Cobalt	0.008			Titanium	0.4	FeS ₂	0.24	8-alumina	0.18		
	Arsenic	0.004									BN	0.03				
	Calcium	0.004									LiCl-KCl	0.38				
	Plastic	0.13									Molybdenum	0.1				
											Yttrium	0.019				
											Cobalt	0.034				

Table 3-2.

Materials for Ten Million Electric Cars in
Relation to Reserves and Resources

Car Range, km	Battery Material	Material as Percent of 1974 Reserves		Materials as Percent of Identified Resources	
		US	World	US	World
100	Lead	4	2	2	1
	Antimony	45	1	35	1
150	Lead	7	2	3	1
	Antimony	74	2	57	1
150	Nickel	--	2	8	1
	Zinc	3	6	1	.1
	Cobalt	--	1	2	.4
300	Cobalt	--	2	6	1
	Lithium	65	30	23	10
	Molybdenum	5	2	.9	.5
	Yttrium	810	74	63	15

Source: Reference 1.

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3.2 Environmental Impacts

3.2.1 Air Quality Impacts

Near-term. The production, use, and recycling of primary storage batteries can involve the introduction into the environment of many substances potentially harmful to plant and animal life, and to human health. Electric batteries are constructed of heavy metals, caustic or acidic materials, and natural materials such as asbestos which represent an environmental hazard. In addition, manufacturing and recycling procedures presently in use or contemplated for near-term battery systems may involve intermediate products or catalytic agents of potential risk. These materials often are formed into battery components by processes leading to fine powders or dust before inclusion in the final product. Usage may involve outgassing from the battery of electrolyte constituents.

Air quality control techniques for the several stages in electric vehicle battery production vary in how well developed they are with the stage of development of the battery system. The component stages leading to lead-acid batteries, for example, are well documented and control techniques are established. Conversely, large-scale production methods for such advanced systems as the lithium-metal sulfide battery are not yet established, hence control techniques are not yet developed; indeed, for such advanced systems, emission types and rates are for the most part unknown.

Far-term. Advanced battery systems, employing highly reactive materials or using electrolytes (such as molten salts) requiring temperatures much higher than ambient, are all in

the early stages of research and development. Full scale production techniques and probable emissions factors are yet to be determined for these systems, although most use materials presently commercially available. Additionally, recycling methodology is yet to be developed.

3.2.1.1 Air Quality Impacts Associated with Mining and Milling Operations

Lead Mining/Milling

Incremental impacts on air quality due to increased lead mining for electric vehicle battery production are expected to be minimal. The reported emission rate for lead particles as a fine dust is $5 \cdot 10^{-5}$ kg/kg (0.1 lbs. per ton) of mined ore (1). For 1973, U. S. production of lead metal was 5×10^8 kg (603,000 short tons) (2). High-grade lead ore may be 10-12% lead by weight (3); taking 8 percent as an average lead content yields an ore weight of 7×10^9 kg (7.5×10^6 short tons).

Projections for lead-acid systems indicate 440 kg (900 lbs.) of lead (as metal and oxide) per battery (4). For a 2,500 vehicle program, at least one million kg of lead will require an additional 1.5×10^6 kg of lead, or about 20 million extra kg of ore. An emission rate of $5 \cdot 10^{-5}$ kg/kg (0.1 lb/ton) of mined ore yields an incremental emission rate of 75 kg, on a base (1973) emission of 3×10^5 kg lead dust emission, for a base-level program of 2500 electric vehicles. Lead is mined at several sites within the U. S. (5), but the preponderance of mining and milling, about 80 percent, is done in Missouri.

Nickel Mining/Milling

U. S. mining of nickel was but two percent of total world production in 1973 (2), and is projected to be only one percent of worldwide production in 1980. For a nickel content per battery of 164 kg (362 lbs.), a total program of 3750 nickel-zinc batteries represents a commitment of approximately six-hundredths percent of worldwide production for an initial-phase EV program. Incremental emissions due to nickel mined in the U. S. for the initial EV program will be minimal.

Zinc Mining/Milling

Zinc is mined primarily for zinc sulfide deposits, often associated with lead deposits. Mining is done by conventional techniques, such as stope and pillar methods. Fugitive dust in the immediate vicinity is likely to be the major air impact. Milling is similarly accomplished by flotation to separate higher-grade ores and roasting (5).

Lithium Mining/Milling

Lithium is mined by either open-pit or subsurface techniques. Little impact from either method on air quality can be expected, other than fugitive dust from pit operations (26).

Lithium beneficiation and milling is primarily by flotation and thermal conversion to a beta-sponge form (26), neither resulting in significant air impacts. The lithium mineral (spodumene, for example) is successively crushed and screened (27), with reagents of high viscosity and low volatility being used for flotation preparation. No gaseous or dust emissions of any significance are present during production of either lithium metal, or of the lithium chloride electrolyte (24, 28).

Sulfur, Iron, Sodium, Zinc Mining/Milling

Present production figures for these minerals are so large and use of their products in the environment so pervasive, that incremental impacts due to mining of materials for inclusion in even a large scale (1 million +) vehicle program will be negligible. Emissions from zinc mining and smelting have been discussed in Section 3.2.1.

3.2.1.2 Air Quality Impacts Associated with Smelting Operations

Lead Smelting

Lead ore, primarily sulfides, is converted to lead oxides and sulfur oxides in a sintering machine (6), then reduced at high temperature to produce lead metal. Large amounts of waste gases containing lead are emitted during this processing, with control devices interposed in domestic plants to control emissions to the atmosphere. An additional source of lead release is storage of lead sulfide concentrate outdoors, where it can be wind-carried into the atmosphere.

Lead, released as particulates, has been estimated at 6.2×10^{-2} kg/kg (124 lb/ton) of concentrated (milled) ore (7); yield ratio of metallic lead is about 1:2 per unit weight of concentrated ore processed. Trace amounts of contaminants such as arsenic and cadmium, found in association with lead, are present as well.

Thus, assuming 3 million kg of concentrated ore will be required for input to the smelting phase for a projected 2500 vehicle program, emissions of two hundred thousand kg (200 short tons) of particulates would result. These emissions will be spaced

out over the production period of the required lead, and are negligible compared to a baseline (1974) emission of 7×10^7 kg particulates emitted from lead smelting. Most such emissions (95+ percent) are controllable by precipitators and baghouses.

More significant are sulfur dioxide emissions, created by the oxidation of lead sulfide in the sintering operation. Overall emission factors of 0.33 kg/kg (660 lb/ton) of concentrated ore have been measured (7); measurements at domestic lead smelters indicate time rates of SO_2 emission of from 8 to 440 tons/day (8). Again, incremental increases due to electric vehicle battery manufacturing on a relative basis are negligible.

Nickel Smelting

Nickel is smelted from ore containing sulfides and oxides through pyrometallurgic or electrowinning processes (9). The larger of two U. S. smelters at Port Nickel, Louisiana, closed in 1960 (9), but reopened in 1974 (2). It treated nickel concentrate with a content of 55 percent nickel, 36 percent sulfur, and the balance primarily other metals. Refining proceeds by solution of the concentrate, precipitating impurities, and producing metal of 99.5+ percent nickel purity. Most waste material comes off as solid (cake or ammonium sulfate) streams.

A typical outgassing from a nickel roaster (9) yields some 2×10^6 kg/day (2214 tons/day) gas, of which some 10 percent is sulfur dioxide. Most of this is diverted to adjacent sulfuric acid plants.

Zinc Smelting

During the smelting of zinc, the principle emissions are particulates, containing zinc sulfides and lead sulfides, and sulfur dioxide. Lead emissions occur due to the common association of lead ore with zinc ore. One estimate (6) is that 4.5×10^6 kg (4900 tons) of lead were emitted in 1970 in association with the 1.4×10^9 kg (1.5×10^6 tons) of zinc ores and concentrates smelted in the United States, an emission rate of 3.3×10^{-3} kg Pb per kg of smelted ore.

Emissions of zinc-containing particulates can be deduced by knowledge of total particulate emissions from a zinc smelter reported at 0.16 kg/kg (321 lb/ton) concentrated ore (7). The particulates appear to be about 98 percent zinc compounds.

For a nickel-zinc battery requiring 149 kg (328 lbs.) of zinc oxide per unit (4), the equivalent is 120 kg (263 lb.) of zinc metal. This requires some 240 kg (526 lb.) ore concentrate (7), or a total of about 1 million kg (2×10^6 lb.), for an incremental emission of about 1.6×10^5 kg particulates. For a total 1974 smelting of 5.75×10^8 kg (633,723 tons) of zinc (2), this is only two-tenths of a percent of total base emissions.

Sulfur oxides represent the major emissions from zinc smelting, reported at some 0.55 kg/kg (1100 lb/ton) ore concentrate (7). Although the incremental effect is small, localized effects due to corrosiveness of sulfur oxides can be significant. Large zinc smelters are located in Texas, Montana, Tennessee, Idaho, and Oklahoma (2), areas subject to atmospheric inversions and likely to suffer adverse effects from sulfur oxide emissions.

Antimony Smelting

Antimony smelting involves roasting with oxygen, which yields a mixture of stable antimony tetroxide and volatile antimony oxide (5). For 2,500 electric vehicles with lead-acid batteries containing 12 kg antimony each (10), plus 50 percent in recycling at any time, this is 3 tenths of a percent of (1973) U. S. smelting. Incremental impacts are likely to be negligible relative to the 1973 base.

Lithium Recovery

The two methods of lithium recovery from concentrate are the acid method and the alkali method (26). Neither method produced significant emissions to the atmosphere. Much information on the lithium industry is proprietary (29), so that detailed data on domestic smelting techniques is difficult to acquire.

Molybdenum Smelting

A pre-vehicle weight of some 20 kg molybdenum (10) in lithium-metal sulfide batteries is conceivable; this represents some 22 percent of projected U. S. molybdenum smelting production in 2000 (5). There is, however, little air quality impact associated with molybdenum smelting.

Sodium and Sulfur Production

Sodium production includes use of ammonia gas, whose control technology is well developed.

Sulfur is one input or by-product in sulfuric acid production, (see Section 3.2.1.4).

3.2.1.3 Air Quality Impact Associated with Battery Production

Lead-Acid Battery Production

Although lead-acid batteries have been in use as primary and secondary power sources for many years, much information on the detailed procedures used by the battery industry in their manufacture remains proprietary. Present battery plants reportedly emit about 2×10^{-3} kg (0.005 lbs.) per battery as lead-containing fumes (1). Another estimate (6) gives an emission factor of 8 lb/ton of lead processed, with controls reducing this to about 1.3 lbs/ton of lead.

A lengthy study of emissions resulting from the present battery industry has been compiled (11) which documents the numerous types of materials emitted. Among the emissions are:

- 0.636 kg/hr (1.40 lb/hr) lead per 1000 batteries from charging and mixing of plate paste.
- 0.835 kg/hr (1.84 lb/hr) of lead for stacking/burning/assembly.

It can be presumed that present emission rates will continue if present manufacturers assemble more advanced lead-acid batteries. Some emission problems of outgassing from electrodes may exist on sealed systems (12), although industry practice has largely solved this problem for present lead-acid cells.

Nickel-Zinc Battery Production

Although no production-scale nickel-zinc battery plant is yet in operation (13), preliminary industrial design studies have been done by potential manufacturers to evaluate likely

procedures for production (14, 15, 16, 17). Much of the detailed information on processes and materials used in production, however, is either not yet determined, or considered proprietary information (18, 19,20).

Air emissions, in-plant, consist of minor quantities of nickel dust (21), most of which is recoverable by air cleaning equipment. A more serious potential problem is the separator material. Present laboratory models use asbestos (20), a toxic material with carcinogenic properties. Although other materials are under development, primarily organic/inorganic combination materials, asbestoc dust in the work place will require close monitoring if asbestos separators are used.

Other potential air emissions include small amounts of ammonia (20), graphite dust (17), about 200 lb/day of evaporated organic solvent (17), and small amounts of nickel hydroxide dust (16). All are unlikely to escape the confines of the manufacturing plant, and recycling is envisioned as recovering most emissions (21).

Charging of batteries will generate hydrogen (4). Battery designs include venting for release, and charging areas of plants used for testing products are planned to be well-ventilated (16).

Oxygen is evolved during charging (12), which is not directly harmful to air quality but does speed "needling" of zinc oxide electrodes and deterioration of battery efficiency.

Nickel carbonyl, a highly toxic carcinogen, has a boiling point of 43°C, and can be formed by passage of carbon monoxide over hot nickel. There is likely to be potential for formation

of the compound, and its boiling to a gaseous form, in the manufacturing plant (18).

Proper ventilation may mitigate this impact although careful monitoring will be necessary to assure acceptable concentration standards are maintained.

Nickel-Iron Battery Production

Substitution of iron for zinc as a battery material is not expected to change the likely air quality impact of the systems.

Hydrogen is evolved during charging (12) when overcharging occurs, hence the battery cannot be sealed. Heat is generated, hence potential exists for hydrogen ignition without proper venting.

The potential for production of volatile nickel carbonyl exists as well for this battery.

3.2.1.4 Electrolyte Production

Sulfuric Acid (for lead-acid battery)

Sulfuric acid production uses raw stock of SO_2 , which is then oxidized and hydrated to form the acid. Although sulfur deposits are tapped for raw stock as well, primarily by the Frasch process (5), sulfur dioxide by product from copper, lead, and zinc smelting provided 6 percent of total U. S. sulfur production in 1974 (2). Electric vehicle battery production's draw on lead and zinc smelting capacity would likely

lead to an increase in the sulfur dioxide stock being drawn from those sources. Presently several zinc and lead plants (8) have acid plants associated with them for production of electrolyte material.

A well-designed plant can convert some 90 to 95 percent of the SO_3 feed stock to acid. Any significant emissions occur after absorption of an SO_2/SO_3 is vented as a fine mist (22, 7), of very small particle size. Assuming a "worst-case" 90 percent conversion rate, the SO_2 emissions are 0.07 kg/kg (135 lb/ton) of 100 percent pure sulfuric acid (7). For a battery electrolyte solution of specific gravity 1.3 (23), the equivalent emissions rate per gram of vehicle electrolyte produced is 2×10^{-4} . For 193 kg (426 lbs) of electrolyte per vehicle, and a base of 2,500 vehicles, total emissions of SO_2/SO_3 will be a 97 kg (213 lbs), a negligible increment.

Potassium Hydroxide (nickel batteries)

Potassium hydroxide concentrate, or caustic, is produced for natural potassium salts (2). Normal production is by electrolysis of potassium chloride (24), naturally occurring in potash deposits. Minor amounts of dust are emitted during the milling stage, but no significant incremental air quality impacts are expected from electric vehicle use.

Lithium-metal sulfur cells have been manufactured by electrochemical changing of lithium onto an aluminum wire structure (30). No significant air quality impacts are foreseeable for the manufacturing stage of these batteries or of the lithium chloride electrolyte. The electrolyte, a

lithium chloride-potassium chloride eutectic, operates at a temperature of 425°C. There is no significant liberation of chlorine gas in the battery system (30).

Other advance systems (sodium-sulfur, zinc-chlorine, iron-air, and lithium-air) have not progressed to a development stage where air quality impacts are identifiable.

Chlorine for use in a zinc-chlorine battery will amount to about 31 kg (69 lb) per battery (4), or, for a base case of five million electric vehicles in the year 2000 (4), a total of some 1.6×10^8 kg (3.4×10^8 lb) of chlorine in use. (This is a lower-limit figure for that number of vehicles). For 1975, U. S. chlorine production was reported at some 8.4×10^9 kg (9.3×10^6 tons); historical growth in chlorine production has been 7 percent per year (5). On that basis, approximately 5×10^{10} kg of chlorine would be produced in the U. S. by the year 2000, of which powered electric vehicle program. Emission factors, presently chlorine gas, CO_2 , CO, and hydrogen, would probably also be negligible in comparison.

3.2.1.5 Recycling

Lead Battery Recycling

Recycling of lead batteries has traditionally been a small-scale manual-labor industry (25) but it is anticipated that large-scale use of lead-acid-powered vehicles will lead to further mechanization and reduction of work-place emissions of lead dust and electrolyte fumes. Once the cases have been crushed, reprocessing proceeds essentially as re-smelting of lead-based components, (see Section 3.2.1.2).

Nickel-Zinc and Nickel-Iron Recycling

It is assumed that any production-stage nickel-electrode battery usage will involve materials that are primarily recycled (21). No reprocessing techniques, however, have yet been formulated, although the nickel electrode made by sintering/impregnation technique can be recycled by a washing process (20). No air quality impacts are expected from recycling, since asbestos separators will be handled wet for recycling.

Nickel carbonyl is a potential problem of some importance, but its magnitude is unknown and cannot be evaluated until further development of recycling procedures (18).

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3.2.2 Water Quality Impacts

Water is an integral component in all phases of the battery production cycle, for mining and milling of the required ores through recycling and disposal. A majority of the waste materials inherent in the processes described in Sections 2.0 and 3.2.1 ultimately are waterborne, and even many of the air pollution control methods utilize water as a solvent. Further, solid waste disposal problems are often exacerbated by the need to avoid water contamination which may occur when precipitation percolates through the hazardous waste material and leaches out heavy metals into a groundwater aquifer, pond, lake, or into the surrounding soil.

The use of water in the battery production cycle is discussed below at a level consistent with the amount of information currently available from manufacturers and in the literature. In many cases, such data is sparse, particularly for the advanced systems, and only qualitative discussions are possible. In fact, the Environmental Development Plan for Energy Storage Systems (1) (schedule for battery environmental research) indicates that an identification and quantification of effluents generated during the manufacture of battery components is not scheduled to begin until sometimes in FY 1978, to be completed in FY 1982. The research, to be carried out by the Biomedical and Environmental Research (BER) Division of the Department of Energy is expected to cover lead-acid, zinc-chlorine, sodium-sulfur, lithium-metal sulfide, nickel-iron, and nickel-zinc batteries.

It is possible to at least characterize the potential water quality problems from the proposed electric vehicle battery systems because many of the processes to be employed are well-

established chemical-industrial technologies. The industries involved are currently regulated or will come under regulation by the Environmental Protection Agency (EPA) under the authority of the Federal Water Pollution Control Act of 1972 (P.L. 92-500). EPA has promulgated effluent limitations for many industries under the Act. At the present time, the two categories of battery manufacturing industries, "SIC 3961--Storage Batteries" and "SIC 3692--Primary Batteries, Dry and Wet", are under study by EPA. According to the consent agreement between (Natural Resources Defense Council) and EPA of June 8, 1978 (8 ERC 2120), proposed regulations for these categories are due by June 30, 1979, and final regulations by Dec. 31, 1979. Such regulations, of course, will cover only existing battery types; effluent limitations for new technologies must await their definition.

Advanced technologies will probably face very stringent effluent standards and if developed after 1985, will be subject to the zero-discharge guidelines of P.L. 92-500. In general, it may be said that the introduction of battery manufacturing technology into today's well-established regulatory scheme, which has been designed to minimize environmental impact, probably mandates that closed-cycle processes be used wherever possible. This is the case for the only near-term (non-lead acid) alternative for which a manufacturing process has been detailed, nickel-zinc, and it appears likely that it will occur for other systems as well. Even with the use of advanced pollution control technology ("best available technology economically achievable"), there will probably be discharges of some pollutants, and makeup water will be required to maintain the closed cycles.

The discussion which follows analyzes the water quality issues from the point of view of existing technology or by using proposed manufacturing processes from the Department of

Energy contractors. For the advanced technologies, only general problems are identified.

3.2.2.1 Water Quality Impacts from Mining, Milling, and Smelting

Mining

The major water quality impact occurring at the mining stage of the battery production cycle is the production of acid mine drainage, and applies to the mining of lead, nickel, zinc, and lead. The first three of these metals are mined predominantly from sulfide ores. For example, about 75 percent of the nickel mined in the world comes from sulfide ores (2). Iron is mined principally from oxide deposits although sulfide ores are significant contributors.

Acid mine drainage is generally formed by the chemical reaction of oxygen (in air), water, and iron sulfide. Microorganisms usually accelerate the chemical reactions. When the iron sulfide is exposed to oxygen, it is oxidized to sulfuric acid and components of iron. The acid and iron are dissolved and the low pH water in turn increases the solubility of other metals and compounds that the water contacts. Therefore, a variety of dissolved ions are usually present in acid mine drainage such as aluminum, manganese, zinc, cadmium, and lead. The most basic characteristic chemical reaction which forms acid mine drainage is the oxidation of pyrite:

Additional details of the chemistry of acid mine drainage may be found in Williams (3).

Acid mine drainage may be characterized by the data presented in Table 3-3. This data was collected for the Bunker Hill Mine in Kellogg, Idaho, the 5th largest zinc producing mine in the U. S. (3). The mine is primarily a lead-zinc mine, with the ore consisting of one-third sphalerite (zinc sulfide). Bunker Hill expects to spent \$750,000 per year to treat the 6000 gpm waste water to EPA standards (Table 3-4) before discharge into the South Fork Coeur d'Alene River. The Coeur d'Alene is a heavily polluted river in northern Idaho, and has been the subject of a number of research studies; the South Fork has been polluted by heavy metals from mining for over 80 years. The Bunker Hill treatment facility is one of a number of proposals designed to help alleviate problems associated with mining industry influent.

It is only possible to characterize the acid mine drainage problem in a general way because there is no fixed volume of water contaminated per unit weight of ore mined. The problem is complex and would be increased by substantial increases in mining of any of the minerals required for battery production. The mining industry is moving away from the old practice of direct release of untreated effluents to receiving waters. Two important regions of the U. S. which could experience an incremental impact from the battery program are the "new lead belt" in Missouri and the previously mentioned Coeur d'Alene region in northern Idaho. A conceptual environmental assessment diagram for mining is shown in Figure 3-1.

The recommended new source performance standards for ferroalloy for mines (5) is given in Table 3-4. It is seen that a substantial amount of treatment of raw mine water will be required, and that not all constituents will be controlled.

Table 3-3* Typical Composition of Acid-Mine Drainage

<u>CONSTITUENT</u>	<u>Concentration¹</u>
pH	2.2
Sulfate as $\text{SO}_4^{=}$	63,000.0
Total iron	16,250
Zinc	14,560
Nickel	4.8
Copper	13.4
Manganese	2,625
Aluminum	347
Lead	0.8
Cadmium	22.5
Magnesium	1,500.0
Calcium	31.6
Potasssium	0.7
Sodium	0.5
Chromium	0.3
Chloride	38.0
Nitrate as NO_3^-	77.5
Electrical conductivity (microhmes @ 25°C)	48,000

*Source (3)

¹In ppm (except pH and electrical conductivity which is in standard units).

Figure 3-1 Conceptual Chart Outlining Steps Needed to Quantify Water Quality Impact of Mining for the Battery Program

Since wastewater volumes from mining are highly variable and uncontrolled, computation of potential incremental impacts resulting from the demands of electrical vehicle batteries is not practical at this time.

Milling

The purpose of milling is to concentrate the metal so that it may be extracted in the smelting process. This consists of a number of steps including crushing, classifying, separating, scavenging, thickening, and filtering. A representative flow diagram from the millint process, that of the International Nickel Co. Copper Cliff mill, is given in Figure 3-2. Water is required for the rodmill, and wastewater associated with the tailings is produced.

The tailings pond is a means of pollution control, while at the same time facilitating the disposal of solid wastes. As an example of the utility of tailings pond, Table 3-5 lists the concentrations of thirteen constituents before and after settling in the tailings pond for a lead-zinc-copper mill. The discharge of the tailings pond effluent to the environment is the present method of disposal, although there has been some attempt to recycle the water back to the milling processes. Problems of such recycle are discussed in (3). Further treatment of the tailing-pond decant usually occurs before discharge if the water is not recycled.

These figures are intended to be representative only, and indicate the parameters which have historically been considered of major significance. EPA, (5), in its development document for the Ore and Dressingindustry point-source category, recommended the following effluent limitations for new source

Table 3-4: Recommended New Source Performance
Standards for Ferroalloy Mines¹

Parameter	CONCENTRATION (mg/l) IN EFFLUENT	
	30-day average	24-hour maximum
pH	6 to 9	6 to 9
TSS	20	30
Oil and grease	3	5
As	0.4	0.8
Cd	0.5	0.1
Cu	0.03	0.06
Mn	0.7	1.0
Mo		
Pb	0.10	0.15
V		
Zn	0.1	0.2
Fluoride	10	20

No limitation proposed for new source performance
standards
¹Source (4)

Figure 3-2 Flowsheet for Copper Cliff Mill¹

ferroalloy mills utilizing the flotation process (Table 3-6). Should the battery system for electric vehicles utilize new mills, these (or similar) figures would apply. Given that the battery systems will have specific material requirements, (summarized in Section 2.0) computations of the effluents of a vehicle program of specific production levels can be performed. Such computations are not meaningful, however, since they do not reflect where the effluent is to be disposed, by what means, and what the ecosystem carrying capacity for the particular effluents are estimated to be. However, such computations would make it possible to estimate environmental impacts on a site-specific basis when actual locations are determined.

Smelting and Refining

The processes included in smelting and refining are charge preparation (blending of the concentrate from milling with siliceous flux), sintering, blast furnace smelting, and refining to remove metallic impurities. The smelting and refining process is similar for lead, nickel, and iron, and water-borne waste products and are discussed in general with specific examples given where data were available to illustrate the problem which must be handled. The zinc processes are somewhat different and they are discussed separately.

Charge preparation produces no waste water. Thus, there is no water quality impact. Sintering is used to remove sulfur from the charge as SO_2 or SO_3 , to eliminate impurities such as arsenic, antimony, or cadmium, and to produce a material of suitable size and strength for melting in a blast furnace. Wastewater is produced from wet scrubbers used in a sulfuric acid plant to which the SO_2 and SO_3 is passed (see Section 3.2.2.5).

Table 3-5 Tailings Pond Decant From a Lead-Zinc Mill*

<u>Parameter</u>	<u>Mill Raw Wasterwater*</u>	<u>Tailings Pond Decant*</u>
pH	8.8	7.8
TSS	248,000	16
COD	488.1	563.5
Oil & Grease	0	6.0
cyanide	0.03	<0.01
Hg	<0.0001	<0.0001
Pb	1.9	0.35
Zn	0.46	0.29
Cu	<0.02	<0.02
Cd	0.005	0.002
Cr	<0.02	<0.02
Mn	0.08	0.28
Total Fe	0.53	0.16

x Source: (3)

* Concentrations in mg/l except pH

Table 3-6 Recommended Effluent Limitations for New Ferro Alloy Mills Using the Flotation Process¹

PARAMETER	CONCENTRATION (mg/l) IN EFFLUENT		WASTE LOAD per unit ore milled			
	30-day average	24-hour maximum	30-day average		24-hour maximum	
			kg/1000 metric tons	lb/1000 short tons	kg/1000 metric tons	lb/1000 short tons
pH	8* to 9*	8* to 9*	-	-	-	-
TSS	20	30	10	20	15	30
Oil and Grease	3	5	1.5	3.0	2.5	5.0
COD	25	50	13	25	25	50
Cyanide	0.02	0.04	0.01	0.02	0.02	0.04
As	0.4	0.8	0.2	0.4	0.4	0.8
Cd	0.05	0.1	0.03	0.06	0.05	0.1
Cu	0.03	0.06	0.02	0.03	0.03	0.06
Mn	0.7	1.0	0.4	0.7	0.5	1.0
Mo	0.5	1.0	†	†	†	†
Pb	0.1	0.2	0.05	0.1	0.1	0.2
Zn	0.1	0.2	0.05	0.1	0.1	0.2
Fluoride	10	20	5	10	10	20

*Value in pH units

† No limitation proposed

¹ Source: Reference 5

In the blast furnace, heat and gases are used to separate the charge produced by the filtering process into molten metal and slag. The slag is sometimes treated to remove any high concentration by-product metals (for example, in a lead smelter, zinc is often obtained from the slag). The final waste slag is usually granulated by impacting it with a high pressure water jet which usually comes from a treated recycled wastewater stream. In Table 3-7, the typical concentrations for the combined waste effluent stream from slag granulation, blast furnace cooling, and miscellaneous blowdown waste streams is given for a lead smelter. In Figure 3-3, a generalized diagram of water use and wastewater sources is a primary lead plant is reproduced. This general diagram is representative of other metal processes as well.

Refining requires no water except for indirect furnace cooling, and therefore produces no wastewater except that used for dust control.

For zinc, the processes involved in smelting are concentrate blending, magnesium removal (if necessary), washing and/or smelting to convert zinc sulfide to zinc oxide, and then leaching with sulfuric acid if electrolyte recovery is used, or pyrometallurgical procedures in lieu of electrolyte recovery.

In concentrate blending and magnesium removal, a number of treatment steps are necessary to prepare the concentrates for roasting. Table 3-8 gives a summary of the effluents associated with these steps.

Roasting is carried out to remove SO_2 and SO_3 , as well as impurities including mercury which enters the waste gas stream. The SO_2 and SO_3 generally enter a sulfuric acid plant

Table 3-7 Characteristics of Combined Waste Effluents From
Slag Granulation, Blast Furnace Cooling Water,
and Miscellaneous Blowdowns¹

<u>Parameters</u>	<u>Total Plant Discharge (mg/l except pH) *</u>
Alkaline	186
COD	8
Dissolved Solids	500
Suspended Solids	36
Sulfate (as S)	215
Chloride	-
Cadmium	-
Copper	0.02
Iron	-
Lead	0.03
Magnesium	-
Nickel	0.04
Zinc	0.50
pH	8.3

¹ Source: Reference 3.

* Plant discharge is about 6×10^6 liters/day

Figure 3-3 Water Use and Wastewater Sources as a Primary Lead Plant¹

¹ Source: Reference 3.

Table 3-6 Pretreatment Effluent Characteristics - Zinc
Concentration ¹

<u>Parameter</u>	<u>Concentration (mg/l except pH)</u>
pH	2.5
Suspended Solids	3,500
Mn	45
Fe	268
Pb	630
Zn	1,275
Cu	1.7
Cd	11.0
Hg	0.02

¹ Source: Reference 3.

where they are removed via scrubbing of the waste streams and are lumped together as acid plant blowdown. The characteristics of such blowdown is given in Table 3-9.

Zinc is produced after washing (or smelting) by either pyrolytic reduction or electrolysis. Table 3-10 summarized the waste streams associated with gas scrubbing from pyrolytic recovery of zinc. Table 3-11 gives similar data for the important steps in the electrolytic process. A summary of water use for primary zinc recovery is shown in Figure 3-4.

The lead, zinc, and iron industries are all regulated by EPA, and all must meet "best practicable" and "best available" treatment technology standards. The battery program would have impacts conforming to the effluent limitations of these industries. Most nickel is mined and milled in Canada, and not subject to U. S. rules and regulations. However, International Nickel Company, Limited, of Canada has recently built a 60 million gallon per day wastewater treatment facility for its Copper Cliff Mill and thus wastewater discharges are controlled in Canada as well. Site-specific impacts can be quantified once actual battery orders are made. Prior to program implementation, reasonable impact projections could be made using statistical techniques however.

Metallic Sodium Manufacture

The manufacturer of metallic sodium is described in detail in Section 2.0. For the Down's cell process, for 648 kg of product, the following waterborne wastes are expected, (4).

Table 3-9 Wastewater Characteristics From Zinc Acid
Plant Blowdown¹

<u>Parameter</u>	<u>Discharge (mg/l except pH)²</u>
Dissolved Solids	5,400
Suspended Solids	200
Cadmium	33
Lead	48
Tellurium	-
Zinc	1,500
CrO ₄	0.10
pH	2.8

¹Source: Ref. 3

² Flow: 1.3×10^6 liters/day

Table 3-10 Gas Scrubbing Wasterwater Characteristics From
Pyrolytic Recovery of Zinc¹

<u>Parameter</u>	<u>Concentration (mg/l)</u>
Dissolved Solids	7.2
Suspended Solids	220
Cadmium	0.15
Lead	58
Cyanide	12

¹Source: Ref. 3

Table 3-11 Effluents From Electrolytic Zinc Recovery Process Steps ¹

<u>Parameter</u>	<u>Recycle Overflow Concentration</u>	<u>Zinc melting casting, and scrubbing</u>	<u>Filter and Dryer Overflow</u>
pH	1.0	6.0	6.0
Suspended Solids	312	22	360
Mn	88	4	7.5
Fe	5.8	0.1	81
Pb	1.8	0.15	79
Zn	5,050	42	200
Cu	0.4	0.1	4.7
Cd	0.1	25	1.5
Hg	0	0	0.02

¹ Source: Reference 3.

Figure 3-4 Wastewater Streams in Primary Zinc Recovery

Source: Reference 3.

1. 50 kg NaCl from the drying process;
2. 4 kg alkaline salts, 60 kg NaCl, and 10 kg calcium plus periodic leaching and cleaning waterwastes from the electrolysis step;
3. 5 to 12 kg waste sulfuric acid from the cooling, curing, and purification step.

In addition, the sodium-calcium sludges are highly reactive when combined with water; therefore, landfill disposal may be unsatisfactory.

3.2.2.2 Water Quality Impacts from Manufacture of Electrolytes

The manufacturing processes for the various electrolytes anticipated for use in the proposed battery systems are described in Section 3.0. Outlined below are the expected waterborne waste product flows, obtained from reference (4).

Sulfuric Acid

The major waterborne wastes are 30 kilograms of sulfuric acid (H_2SO_4) and sulfurous acid (H_2SO_3) mixed in a dilute solution from the scrubber in the contact process, produced per 1,000 kg sulfuric acid product. In the alternative process, called the Chamber process, leaks and spills of about 200 kg per 1,000 kg product are common. Most smelters today also produce sulfuric acid as a by-product. Since the acid is easily neutralized and it is thus not a difficult problem except for possible excess solids concentrations.

Chlorine

There are three processes used to produce chlorine today although the second of these to be discussed is being phased out due to problems as waterborne waste products per 1,000 kb chlorine product.

In the Diaphragm cell process, 36-265 kg NaCl, 15 kg NaOH, 0.04 kg lead, 0.1 kg asbestos, 0-20 kg Na_2SO_4 , and 0.01 kg copper are produced as waterborne waste products per 1,000 kg chlorine product.

This waste stream required extensive treatment for removal of the toxic substances.

In the Mercury Cell process, 800 kg of wastewater contains about 1 kg suspended solids, 87 kg NaCl dissolved and traces of mercuric chloride complex, (HgCl_4^{2-}) . The mercury concentration of wastewaters is to be reduced to 0.00014 kg/kg chlorine by the end of 1977 and to near zero by 1983. This process is being phased out in some locations, largely due to the problems associated with the disposal of mercury-containing wastes.

The third process, the Down's Cell process, is also used to produce metallic sodium. The waterborne wastes produced in this process were discussed in Section 3.2.2.1.

Potassium Hydroxide

This is produced as a by-product in chlorine manufacture described above.

Bromine

Bromine is produced in a closed-cycle process which produces no waterborne wastes. Natural brines are required as a water source.

Potassium Chloride

Potassium chloride is produced in a process in which no water effluents are released since all materials flow through evaporation ponds. The manufacture of potassium chloride occurs in an arid region of New Mexico.

Zinc Chloride

No wastewater is produced in zinc chloride manufacture although some process water is required. The exact volume is not significant, and therefore is not addressed by EPA in its "Assessment of Industrial Hazardous Waste Practices" (4).

Beta-Alumina

Very little definitive information regarding this material has been found to date, hence wastewater produced can not be addressed.

Lithium Chloride

Lithium chloride is produced from spodumene ore via the intermediate steps of lithium sulfate and lithium carbonate production. The chemical reactions involved are:

No information was available on waste streams from these reactions. Presumably, there are several waterborne waste streams from steps (2) and (3). Further investigation is necessary.

3.2.2.3 Water Quality Impacts from Battery Manufacture

The battery industry is currently under study by EPA for the purpose of developing effluent limitations and new source performance standards. Only two battery systems under study by EPA are also intended for electric vehicle usage: lead-acid and lithium batteries. For the remaining battery systems, estimates of wastewater quantities and constituents were obtained from DOE contractor proposed manufacturing processes. Since most of the advanced battery research is still in the laboratory stage, it is difficult to discuss wastewaters generated by manufacturing.

Lead-Acid Battery Manufacture

In the lead-acid manufacturing plant, the following sources of wastewater have been identified by EPA (7).

- paste mixing and pasting area washdown;
- acid mixing area washdown;
- contact cooling water use after acid filling or during formation;
- oxide production area wet scrubbers,

- oxide production area washdown;
- battery rinse after acid fill or dump;
- dry charge plate wash;
- dry charge formation area washdown;
- final battery wash;
- production area washdown; and
- wet scrubbers for dust control.

For the plants that were studied by EPA, the following ranges of important pollutants were observed:

Water Borne Pollutant	Amount, kg/kg (except pH) <u>Range</u>
Lead	0.0052-0.61
Iron	0.0045-0.063
Oil and grease	0.0094-0.092
Total suspended solids	0.027-0.20
pH	1-7

The distribution of total water discharges from lead-acid battery plants is summarized in Figure 3-5. This Figure may be interpreted by considering one example. Eighteen percent of all discharges consists of 2,000 liters/kg of product or less. Such distribution curves make it possible to quickly examine the range of water discharges from the different manufacturing processes.

By December 31, 1979 EPA is expected to promulgate effluent guidelines and new source performance standards for lead-acid batteries. Until then, it is expected that the current plants will be utilized with their accompanying pollutant loadings for near-term electric vehicle production.

A number of treatment systems are currently used for lead-acid battery plants. These are summarized in Section 2.0.

Figure 3-6 Distribution of Total Water Discharge from Lead-Acid Battery Plants

Source: Reference 4.

After treatment, the final effluent is disposed into an adjacent river, sanitary sewer, percolation pond, the ground, or into a containment pond, dependent upon which plant is considered. Significant localized impacts may result from these practices.

Nickel-Zinc

Nickel-zinc batteries are described in detail in Section 2.0 of this report. The preparation of electrodes is the likely source of wastewater which will require treatment before recycle or disposal.

In the preparation of the positive electrode, (the nickel-oxide electrode), water is used in a number of rinse steps. A nickel plaque is formed in the first step of the process (8). This plaque is treated with potassium hydroxide followed by four rinse cycles with demineralized and deionized water. It is assumed that rinse water is treated and recycled. In Figure 3.6, a proposed system for collection and treatment of effluents, designed by Yardney (9) is outlined for all wastewaters generated in the production process. Final effluents from this treatment process include nickel, cobalt, cadmium, nitrate, chloride, and sulfate. Yardney claims that this treatment system will meet State of Connecticut water discharge standards for heavy metals. EPA has allowed discharge of up to 1.7 kg/day of nickel and 0.28 kg/day of cadmium in an NPDES permit for a nickel-cadmium plant which is effective through February, 1980. New nickel-zinc plants will probably have more stringent limitations, although none have been developed at this time.

The negative electrode, (made of zinc), is to be manu-

Figure 3-6 Proposed Batch Collection and Treatment of Effluents from Yardney's Nickel-Zinc Facility - Schematic Program ¹

¹ Source: Reference (9)

factured by a water slurry method. Wastewater is generated by this process, with zinc being the main contaminant in the wastewater. Few details are available.

Wastewaters will also be generated in the assembly process. The industry has substantial experience in nickel-cadmium battery production and it is anticipated that many of the abatement measures and wastewater loadings will be similar.

Nickel-Iron

Waste streams for nickel-iron batteries have not as yet been fully described. The wastes produced are expected to be similar to nickel-zinc, except that the negative electrode, which is made from iron, will probably have a wastewater stream heavily acidic and concentrated with several species of iron.

Lithium-Metal Sulfide Battery

This new manufacturing process is not as yet detailed enough for the establishment of the wastewater streams that would be produced. However, EPA (7) does treat lithium batteries briefly in its discussion of the battery industry. Lithium battery manufacture consists of preassembly of nickel-plated steel cans, preparation of cathode and anode, cell assembly, testing, and packing. Water is used in cathode preparation. In one plant for which data was made available, EPA reports that 6.6×10^5 liters of water are used per metric ton of product. In addition, the waste stream from this plant contained from 0.007 to 1.9 kg of lithium per kkg of product, and averaged 22 kg/kkg product total suspended solids. The

lithium industry is generally very reluctant to release any additional details on its production methods, and the advanced design for the lithium battery may be quite different from the present plants.

Other Battery Systems

Only very sketchy details are available for the other advanced systems. Water quality problems are outline in the Environmental Development Plans for Energy Storage Systems and Electric Vehicle Systems (1, 6). These are very general and will remain so until specific manufacturing processes are proposed.

Literature Cited in Section 3.2.2 -
Water Quality Impacts

1. Energy Research and Development Administration, "Environmental Development Plan (EDP) - Energy Storage Systems," ERDA Office of Assistant Administrator for Environment and Safety, Office of Assistant Administrator for Conservation, September, 1977.
2. Boldt, Joseph R., Jr., The Mining of Nickel, Its Geology, Mining, and Extractive Metallurgy, Longmans Canada, Limited, Toronto, Ontario, Canada, 1967, 487 pp.
3. Williams, Roy E., Waste Production and Disposal in Mining, Milling, and Metallurgical Industries, Freeman Publications, Inc., New York, NY, 1975, 489 pp.
4. U. S. Environmental Protection Agency, "Assessment of Industrial Hazardous Waste Practices, Inorganic Chemicals Industry," EPA Office of Solid Waste Management Programs, Hazardous Waste Management Division, 1975.
5. U. S. Environmental Protection Agency, "Development Document for Effluent Limitations Guidelines and Standards of Performance for the Ore Mining and Dressing Industry Point Source Category (Draft)," EPA, Office of Water and Hazardous Materials, Effluent Guidelines, April 1975.
6. Energy Research and Development Administration, "Environmental Development Plan - Electric Vehicle Systems - FY 1978," ERDA Office of Assistant Administrator for Environment and Safety; Office of Assistant Administrator for Conservation, August, 1977.
7. U.S. Environmental Protection Agency, "Development Document for Proposed Effluent Limitations and New Source Performance Studies for the Battery Manufacturing Point Source Category (40 CFR 761)," EPA Office of Water Planning Standards, Effluent Guidelines Division, 1977 (in preparation).
8. Eagle Picher Industries, Inc., "Design and Cost Study for Nickel-Zinc Battery Manufacture - Electric Vehicle Propulsion Batteries," Eagle Picher Industries, Inc., Electronics Division, Joplin, Missouri, 1976.
9. Yardney Electric Corporation, "Final Report - Design and Cost Study - Zinc-Nickel Oxide Battery for Electric Vehicle Propulsion," Yardney Electric Corporation, Yardney Electric Division, Pawtucket, Rhode Island, October, 1976.

3.2.3 Solid Waste Impacts

3.2.3.1 Summary

Many component materials used in the candidate batteries are potentially hazardous or dangerous. Certain amounts of these hazardous materials will become solid wastes during battery manufacture and at the end of the useful life of the battery. The generated solid wastes may become a source of environmental and health problems.

The extent of potential environmental impact of the generated solid wastes depends upon the waste disposal method and waste composition. In current practices, solid wastes (waste rocks, tailings and slags) from the related mining, refining and smelting processes are generally used to refill the mining sites or dumped on vacant lands. Landfill is commonly used for disposing of solid wastes (scrapes, rejected materials, sludges, etc.) from the battery manufacturing processes. Solid wastes (discarded cases, separators, sludges, etc.) from recycling and disposal of worn-out batteries may enter into municipal waste streams or may be deposited at industrial waste disposal sites. Hazardous wastes washed from the dump sites and/or leached out of the landfill sites are potential sources of environmental impact.

Hazardous materials which may be found in the generated solid wastes vary with battery systems.

Hazardous materials which may be found in the candidate batteries are listed below:

<u>Battery</u>	<u>hazardous substances</u>
Lead-Acid	elemental lead lead sulfate lead sulfide sulfuric acid
Nickel-zinc	potassium hydroxide nickel hydroxide
Nickel-Iron	potassium hydroxide nickel hydroxide
Zinc-chlorine	chlorine zinc chloride
Zinc-Bromine	zinc bromide
Lithium-metal sulfide Lithium-H ₂ O-air	lithium (reacts violently with water)
Sodium-sulfur	sodium (reacts violently with water)
Iron-air	potassium hydroxide
Zinc-air	potassium hydroxide

As many of the candidate battery systems are still in the development stages, the amounts of hazardous materials which may enter into the solid wastes streams cannot be determined at the present time.

3.2.3.2 Solid Wastes from Mining, Milling and Smelting of Primary Metals (excluding Metallic Sodium)

The principal metals to be used in the candidate battery systems include lead, zinc, nickel, iron, lithium, and sodium. Small amounts of other metals (such as antimony titanium etc.) are also used in the batteries to improve electrode performance. Except for the metallic sodium which is currently produced from salt, the production of required primary metals involves mining, milling, smelting and refining of ores. Although the detailed mining, milling, smelting and refining processes for these metals vary, there are certain common types of process solid wastes. This includes waste rocks from mining operations, tailings from milling and concentrating operations, and slags from smelting operations. Much of the generated solid wastes contains hazardous materials such as lead, antimony, sulfur, etc. and is generally deposited on land. The accumulation of this solid wastes may result in denudation of land, alteration of surface and subsurface drainage patterns, clogging of stream channels, flooding, water pollution, air pollution and general disruption to the total ecological system. The incremental demands of raw materials by the electric vehicle battery program will probably increase the solid waste problems of the mineral production industry. The following paragraphs discuss the three common types of solid wastes and the associated environmental problems.

Waste Rock

Waste rocks are produced during the exploration, development, and mining of ore deposits. The amount of waste rocks generated depends upon the age of the mine,

composition and structure of ores, and other factors. The waste rocks generated from mining the required metals are summarized in Table 3-12.

As can be seen, huge amounts of waste rocks are generated by the industries annually. The waste rock is either disposed of in waste rock piles, used for construction of tailings dams and mine roads, disposed of in the tailings ponds, or crushed for use as mine backfill. The major problems associated with waste rocks are the alteration of surface drainage patterns and the sedimentation from storm runoff associated with surface mines. This may result in local flooding or clogging of stream channels. The pollution impacts of the generated waste rocks are usually not significant because the mineral contents of the waste rock are generally similar to those of background environment.

Tailings

In the mining and milling process, the mined ores are crushed and ground and then sent through a process to produce concentrates. The tailings generated from this operation have a high potential for adverse pollution impacts as tailings usually contain various hazardous materials such as heavy metals and their compounds, sulfur, etc. The quantities of tailings generated vary with ore grade and the percent of metals present in the ore. Whether a mine is dry or wet also greatly affects the quantity of tailings generated. The tailings generated from related mining industries are briefly described in Table 3-12.

In general practices, the tailings are disposed of in tailings ponds. For wet mines (mines below ground water table), acid mine water is first discharged to the tailings

ponds. The water from the tailings pond is then pumped to a dispersion pond or wastewater treatment plant before being released to a river. The sludge from the treatment plant is generally pumped back to the tailings pond. For relatively dry mines, a tailings pond functions as a landfill site. When a tailings pond is full, it is vegetated with native trees, shrubs and grasses. In the past, tailings were also dumped into lakes at some mines.

The environmental impact of the generated tailings depends upon the disposal methods and the chemical composition of the tailings. In general, the tailings contain various heavy metals, salts, acids or bases and synthetic organics (agents used in the concentrating process). Table 3-13 shows the chemical analysis of sample tailings from lead-zinc mines and the concentrators. These materials are potentially hazardous. The land disposal of tailings would have significant environmental impacts if the hazardous materials leach out of the tailings pond. This is particularly critical in the wet mines where the acid mine water is discharged to a tailings pond. The acid mine water (pH 2 to 2.5) lowers the pH of the tailings slurry below 6. The solubility of most heavy metal salts increases as the pH of the contacting water is below 7. Pumping of unneutralized acid mine water to the tailings pond would have negative environmental impacts on the surrounding groundwater and surface water quality. The dumping of tailings directly into water bodies such as a lake, pond or river would have adverse environmental impacts; this practice is prohibited almost in every state now.

Table 3-12 General Description of Major Solid Wastes Generated from Related Metal Mining Industries

PRINCIPAL METALS REQUIRED	RELATED BATTERY SYSTEMS	TYPICAL WASTE ROCKS GENERATED	TYPICAL TAILINGS GENERATED	TYPICAL SLAGS GENERATED
Lead	Lead acid battery	0.1 ton of waste rock per ton of lead-zinc ore mined (1)	dry mine: 0.26 to 0.96 ton of tailings per ton ore mined wet mine: 1.73 to 2.79 ton of tailings per ton ore mined (1)	32 million tons of lead-zinc smelter wastes had been accumulated up to 1968 (2)
Zinc	Nickel-zinc battery Zinc-air battery Zinc-chlorine battery Zinc-bromine battery	0.02 ton of waste rock per ton of zinc ore mined (1)	dry mine: average ratio of tailings to ore mined = 0.132 ton/ton wet mine: average ratio of tailings to ore mined = 2.72 ton/ton (1)	32 million tons of lead-zinc smelter wastes had been accumulated up to 1968 (2)
Nickel	Nickel-iron battery Nickel-zinc battery	0.16 ton of mine waste per ton of ore mined (2)	approximately 2000,000 tons of tailings generated in 1968 (2)	1 million ton of nickel slag was produced in 1967 (2)
Molybdenum	Lithium-iron sulfide battery	25,000 ton of waste rocks generated in 1967	19,000 tons of milling wastes generated in 1967	not available
Lithium	Lithium-metal sulfide battery Lithium-H ₂ O-Air battery	not available mining process and related information are proprietary	not available (proprietary information)	not available (proprietary information)
Iron	Iron-air battery	up to 1968, approximately 190 million tons of mine waste accumulated in 600 mine dumps (2)	720 million tons of tailings accumulated up to 1968 (2)	0.5 ton of slag per ton produced
Titanium	Zinc-Bromine	all waste products are reportedly returned to the mine sites	<0.001 ton of oversize ore/ton of ore mined	0.08 ton/ton of product
Sodium	Sodium-sulfur	not applicable metallic sodium is produced by electrolysis of molten salt (4)	not applicable	not applicable
Antimony	Lead-acid battery	0.04 ton of waste rocks per ton of ore mined	0.15 ton of wet tailings per 1 ton of ore mined	Most of the antimony comes as coproduct of other metals. Because of the close mineralogical association with lead, antimony is extracted at primary lead refineries. The slags are attributed to lead refineries.

Table 3-13. Analysis of Tailings from Lead-Zinc Mines and Concentrators
(Concentration in ppm)

Element	Concentrator 1	Concentrator 2	Concentrator 3	Concentrator 4	Background
Calcium	1,549	3,279	2,524	1,598	1,500
Cadmium	8.5	6.3	19.2	20.9	--
Copper	71.6	72.5	136	117.8	21
Iron	76,708	59,813	88,917	113,667	11,800
Potassium	335	406	422	287	1,800
Magnesium	2,460	2,482	3,781	2,680	3,700
Manganese	5,527	5,932	9,123	10,154	490
Sodium	92	69	75	69	151
Lead	2,302	2,624	4,380	4,462	51
Antimony	365	360	390	1,463	--
Zinc	2,057	1,316	3,547	3,366	150

Source: Reference 1

Slags

Slag is a by-product waste of the smelting process which converts ores or concentrates into the metals. The slags generated from the smelting processes of battery metals are also summarized in Table 3-12.

Most of the metal slags generated from the metal industry are dumped on land. These waste piles are often extremely unsightly. More importantly, the leachates from a slag pile may contribute significantly to both surface and groundwater pollution. Loss of vegetation and aquatic life resulting from adjacent lead slag piles has been reported (3). More studies need to be conducted to determine the environmental effects of other metal slags.

Because of the potential environmental problems and the land requirements for the disposal of metal slags, metal industries have been investigating ways of using the generated slag. The slags from lead and zinc smelters can be used as construction aggregates, as are the slags from iron smelters. Slags from nickel smelters have been partly used as fertilizer. Reuse of the discarded slag is one of the measures to minimize the disposal impacts.

3.2.3.3 Solid Wastes from Metallic Sodium Production

As noted previously, metallic sodium is produced primarily by electrolysis of molten salt, i.e., the Down's Cell process. This process also produces chlorine as a co-product.

In this process, sodium chloride brines are first purified to remove calcium and magnesium salts and sulfates.

Then the sodium chloride is dried and fed to the cell to mix with calcium chloride and other minor bath components to form a low-melting $\text{CaCl}_2\text{'NaCl}$ eutectic. After electrolysis of the molten salt, sodium is formed at one electrode and chlorine is liberated at the other. Figure 3-7 shows a simplified process flow diagram for this operation. The material balance including generated wastes is also indicated in Figure 3-7.

For 648 kgs of sodium product, the following major wastes are generated by the process:

- 4 kgs of brine purification muds. - These generally contain calcium carbonate, magnesium hydroxide and in some cases barium sulfate.
- 13 kgs of Sodium-calcium sludges from filtration of product sodium. - These wastes are considered hazardous because sodium reacts vigorously with water. Adequate disposal controls must be made to avoid fires or explosions.
- Wastes from cell maintenance and replacement, including 4 kgs of alkaline salts, 60 kgs of salt, and 10 kgs of carbon and rubble contaminated with sodium. The sodium containing wastes should be kept in the open in an isolated area exposed to the weather so that moisture can penetrate and react with the sodium.

3.2.3.4 Solid Wastes from Manufacture of Electrolytes

Table 3-14 indicates the electrolytes used in the candidate battery systems. The processes for manufacturing these electrolytes generate certain types of solid wastes. The generated solid wastes usually contain various hazardous materials, posing potential environmental problems.

Figure 3-7 Sodium and Chlorine Manufacture Down's Cell Process

Source: Reference 4.

Table 3-14 Solid Wastes from Manufacture of Electrolytes

Electrolyte	Battery Systems	Solid Wastes Generated
Sulfuric Acid	Lead-Acid	Sludge from alkaline scrubbing of tail gases; sludges from neutralization process of product leaks and spills.
Zinc Chloride (Chlorine)	Zinc-Chlorine	<p>Diaphragm Cell Process:</p> <p>Brine purification muds: 15 (units: Kg/1000 Kg product)</p> <p>Sludge from Wastewater Treatment:</p> <p>0.04 lead, 10 Na_2SO_4, 35 to 265 NaCl, etc.</p> <p>Asbestos Wastes from Cell Diaphragms:</p> <p>0.4 asbestos; 3 carbon and rubble.</p> <p>Drummed Waste: 0.45 Chlorinated hydrocarbons.</p> <p>Mercury Cell Chor-Alkali Process:</p> <p>Brine purification muds: 0.005 kg/1000 kg product</p> <p>Sludge from wastewater treatment plant:</p> <p>0.050 mercury, 87 NaCl</p> <p>Drummed Wastes: 0.1 chlorinated hydrocarbons</p> <p>Down's Cell Process:</p> <p>4 Brine purification mud 50 solid waste 10 carbon and rubble wastes 13 sodium calcium sludge</p>
Potassium Hydroxide	Zinc-Iron Zinc-Air Iron-Air Nickel-Zinc	This product is produced solely as a co-product of chlorine manufacture. The solid wastes generated are discussed in the manufacture of chlorine.
Zinc Bromide (Bromine)	Zinc-Bromine	No solid wastes generated from manufacture of Bromine from Brine.
β -Alumina	Sodium-Sulfur	Information on solid wastes from the current ceramic fabrication processes are not available; more economic manufacturing process is being developed.
Potassium Chloride -eutectic	Lithium-Metal Sulfide	<p>Tailings waste and brine: 2500-3750 kg NaCl/1000 kg of product <100 Flotation chemicals</p> <p>Slimes to waste: 75 clay</p>
Lithium Chlorine -eutectic	Lithium-Metal Sulfide	No information available.

The solid wastes associated with the manufacture of each of the electrolytes are summarized in Table 3-14. More detailed descriptions of the associated solid waste problem are presented in the following paragraphs. It should be noted that only the principal processes for manufacturing the electrolytes were considered. The solid waste problems associated with processes or industries which produce by-product electrolytes were not considered.

Sulfuric Acid

Sulfuric acid is produced primarily from the contact process in the U.S.; Sulfuric acid is also produced as a by-product from oil refining and non-ferrous metal industries. In the contact process, purified and dry sulfur dioxide is mixed with air, heated and introduced into a reactor containing a platinum or vanadium pentoxide catalyst. The resulting gas mixture is then cooled and purified. The battery acid (33.5% H_2SO_4) as well as 98% percent concentrated sulfuric acid can be produced by this process. The process flow diagram is shown in Figure 3-8. The major solid wastes generated are the sludges from alkaline scrubbing of tail gases and neutralization process of product leaks and spills. The generated sludge must be carefully disposed of to avoid any adverse impact on the environment. As the semi-solid sludge can be hardened (fixated) through chemical reactions to form a dry, solid, largely inert material or it can be ponded; the environmental impact of the generated sludge should not be adverse.

Figure 3-8. Sulfuric Acid Manufacture by the Contact Process

Chlorine

Chlorine is currently produced by the following three major processes:

- (a) The Diaphragm Cell Chlor-Alkali Process; which also produces sodium hydroxide as a co-product.
- (b) The Mercury Cell Chlor-Alkali process in which sodium hydroxide or potassium hydroxide is produced as a co-product.
- (c) The Down's Cell Process, which involves the electrolysis of molten salt and produces metallic sodium as a co-product.

In addition, the Kel-Chlor and Vicksburg chemical processes are currently operational at two facilities. Some quantities of by-product chlorine are also produced by the electrolytic manufacture of magnesium.

The solid wastes associated with the above mentioned three major processes are discussed below.

1. Diaphragm Cell Process

In this process, sodium carbonate, flocculating agents and sodium hydroxide are added to the natural brine to remove all the magnesium and calcium contents of the brine. The insolubles formed are then filtered and electrolyzed in a diaphragm cell. Chlorine, formed at one electrode, is collected, cooled, purified and compressed. The sodium hydroxide, formed at another electrode, is subjected to partial evaporation to purify sodium hydroxide and recover salt. The collected salt is recycled in the process and

the sodium hydroxide solutions are further evaporated to yield solid products. Figure 3-9 shows the process flow diagram for a typical operation. The material balance as well as the major solid wastes generated are also indicated in Figure 3-9.

As shown, for 1000 kg of chlorine product, the following solid wastes are generated:

- 15 kg of brine purification muds. - Contains calcium carbonate, magnesium hydroxide, barium sulfate and water.
- 3 kg of carbon and rubble and 0.4 kg of asbestos from electrolysis process. - Asbestos is a known carcinogen.
- Sludge from wastewater treatment. - This sludge contains toxic lead carbonate and basic lead carbonate from the corrosion and breakdown of the diaphragm cell. The amount of sludge generated is affected by the degree of water treatment.
- 0.45 kg of chlorinated hydrocarbon wastes generated from purification of chlorine gas. - May contain toxic chloroform, carbon tetrachloride and others.

The generated solid wastes contains certain amounts of toxic materials such as asbestos, lead carbonate, and chloroform. Land disposal of these wastes is currently used by the industry. Safeguards must be provided to prevent these toxic substances from leaching out of the site.

Figure 3-9 Chlor-Alkali Manufacture Diaphragm Cell Process

Source: Reference 4.

2. The Mercury Cell Chlor-Alkali Process

This process produces chlorine and caustic soda if brine is used as the raw material, and chlorine and caustic potash if potassium chloride is used instead. In this process, the raw material is first purified by addition of barium carbonate, soda ash and lime to precipitate magnesium and calcium salts and sulfates. The insolubles formed are then filtered and electrolyzed in a mercury cell. Chlorine is then formed at one electrode and a sodium-mercury amalgam is formed at the other. The chlorine is collected, cooled, purified and compressed. The mercury-sodium amalgam is treated to produce sodium hydroxide and hydrogen, and recover mercury for recycling. Figure 3-10 shows the typical process flow diagram, material balance and generated solid wastes.

For 1000 kg chlorine product, the process produces the following wastes:

- 17 kgs of brine purification muds. - These are often contaminated with mercury in a typical amount of 0.005 kg per 1000 kg of chlorine product.
- Sludges from treatment of brine to remove mercury components. - This may contain elemental mercury and mercury sulfide in the amount of 0.058 kg per 1000 kg of chlorine produced.
- 0.1 kg of chlorinated hydrocarbons from chlorine purification.

Among the wastes generated, the sludges from mercury removal treatment and chlorinated hydrocarbons wastes have a high potential for contaminating the surrounding soils and groundwater if they leach out of the landfill sites. The toxicological effects of these hazardous materials are discussed in other sections of this report.

Figure 3-10 Chlor-Alkali Manufacture Mercury Cell Process

Source: Reference 4.

3. The Down's Cell Process

Chlorine and metallic sodium are produced as co-products by this process. The wastes associated with the process have been addressed in the manufacture of metallic sodium. (Figure 3-7).

Potassium Hydroxide

Potassium hydroxide is produced solely as a co-product of chlorine manufacture. In the mercury cell and diaphragm cell chlor-alkali process, both chlorine and potassium hydroxide are produced if potassium chloride is used as raw material instead of brine. The wastes generated have been discussed in the manufacture of chlorine, (Figures 3-9 and 3-10).

Bromine

Natural brines are used as raw materials to produce bromine. In the manufacturing process, chlorine gas is added to natural brines to oxidize the bromide ions contained in brines to free bromine. The crude bromine is then cooled and purified. A typical manufacturing process is shown in Figure 3-11. As the spent brines are recycled in the process, there are no solid wastes generated.

Potassium Chloride

Potassium chloride is produced from either natural brines or sylvinitic ores. In the natural brine process, there are no hazardous wastes generated since the spent brine is recycled in the process.

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Figure 3-11. Schematic Flow Diagram for the Separation of Bromine from Brine (ref. Assessment of Industrial Hazardous Waste Practices, Inorganic Chemicals Industry; U.S. EPA, 1975).

The process for manufacturing potassium chloride from sylvite ores is illustrated in Figure 3-12. For 1000 kgs of potassium chloride product, the following solid wastes are generated by the process:

- 75 kgs of clay and other undissolved materials from settling tanks.
- Wet tailings wastes including 2500 to 3750 kgs of salt and less than 100 kgs of flotation chemicals (tallow amines, polyalkyl glycol starch, etc.).

These wastes are not considered hazardous and can be deposited in a landfill.

Zinc Chloride

Zinc chloride is prepared by reaction of zinc oxide with hydrochloric acid. Figure 3-13 shows the typical manufacturing process for zinc chloride. As can be seen, one to 10 kg of solid waste is generated from the product purification process. These wastes are usually sold for reclaiming lead and cadmium and are not discarded. Thus, there is no solid waste-impact associated with manufacture of zinc chloride for a zinc-chlorine battery.

B-Alumina

Process information is unavailable at this time.

Lithium Chloride

Process information is unavailable at this time.

Figure 3-12. Potassium Chloride Manufacture From Sylvite Ore.

Source: Reference 4

3.2.3.5 Solid Wastes From Battery Manufacture

Lead Acid Battery

Figure 3-14 shows a typical process flow diagram for the manufacture of a current day lead-acid battery (5). The material flow balance based upon 1000 mass units of dry battery product is also indicated in the diagram. The sources, quantities and disposition of solid wastes from manufacturing processes are summarized in Table 3-15. Only the waste generated by the manufacturing processes is considered. The non-process waste generated in the form of rubbish is not considered in this study.

As can be seen, all solid wastes excluding wastewater treatment sludges are recycled directly to the manufacturing facilities, reclaimed in the plant, or shipped to a smelter. The wastewater results from the pasting area, the dry and wet charge forming areas, and the assembled battery washing area. The wastewater streams contain sulfuric acid, and dissolved and suspended lead. The quantity of generated wastewater ranges from 42 to 290 liters per conventional battery produced; depending upon whether the dry or wet charge production process is used. The generated wastewaters are usually neutralized by treatment with lime or caustic soda. Approximately 20 percent of the existing battery plants in the U.S. use lime neutralization treatment and 80 percent use caustic soda treatment. Lime neutralization treatment produces much larger amounts of sludge than does caustic soda treatment. Caustic soda treatment is more costly than lime neutralization. Sludges from both neutralization methods contains lead hydroxide, lead sulfate and others, and are deposited in landfill. The typical composition of sludge based upon production of 1000 kg of batteries is shown in

Figure 3-14. Major Production Operations in Lead-Acid Storage Battery Manufacture

Table 3-15 Sources, Quantities, and Disposition of Waste Materials (Metric Units) from Battery Manufacturing Processes.

Type of Waste	Source	Quantity (kg/1000 Kg of Dry Battery)	Disposition
Dusts, dross, and rejected materials	Grid manufacturing	30 kg Pb	Reclaim
Lead and lead oxide paste	Paste preparation	2 kg Pb/PbO	Reclaim
Lead and lead oxide in rise waters	Pasting area	5 kg Pb/PbO in 1% solution	Wastewater treatment
Projected plates	Plate curing	10 kg PbO 20 kg Pb	Reclaim
Rejected assembled elements	Three-process	10 kg PbO 20 kg PbO	Reclaim
Raw wastewater solutions	Pasting area formation battery rinsing	10.5 m ³ 2-4% H ₂ SO ₄ 0.33 kg Pb	Wastewater treatment
Sludges	Wastewater treatment	Caustic neutralization - 0.54 kg Lime neutralization - 735 kg	Landfill
Air contaminants	Total plant	< 0.1 kg Pb/PbO	Reclaim

Source: Reference 4.

Table 3-16. These lead compounds are among the most hazardous of the toxic metals. The disposal of the generated sludges would have adverse environmental impacts if the lead compounds were to leach out of the disposal sites. The massive production of lead-acid batteries for electric and hybrid vehicles will substantially increase the quantity of lead containing sludge. As the hazardous sludge is usually deposited in a landfill, there is a high potential for lead contamination to the environment.

Among the lead compounds contained in the sludge, lead sulfate has a water solubility of 42.5 mg/liter at 25°C, and lead hydroxide has a water solubility of 150 mg/liter. These lead compounds may leach out of disposal sites into surrounding ground and surface water and soils. Once lead salts enter the surrounding environment, they tend to concentrate through both aquatic and terrestrial food chains. Lead concentration in aquatic macro- and micro-flora and fauna was found to be higher than that in the surrounding environment. Fish and insects retain lead in their tissues when they consume those macro- and micro-organisms. Plants also accumulate lead from surrounding soils. Subsequently, these organisms are consumed by larger organisms, and this process continues to the organisms at the top of the pyramidal food chain, such as man and large carnivorous birds and mammals. An excessive level of lead in the human body can cause anemia, severe intestinal cramps, and more severely, brain and nerve damage and death. A more detailed description of the toxicological effects of lead and its compounds are given in other sections.

Nickel-Zinc Battery

The manufacturing processes for the nickel-zinc battery projected by DOE contractors have been described in detail

Table 3-16 Composition of Sludge from a Typical Lead-Acid Battery Plant

1. Sludge from Lime Neutralization Treatment

CaSO_4	= 2101 kg per 1000 kg Batteries (35 percent solids)
Pb(OH)_2	= 0.140 kg per 1000 kg Batteries
PbSO_4	= 0.293 kg per 1000 kg Batteries
Pb	= 150 mg per liter

2. Sludge from Caustic Soda Treatment

total sludge	= 0.541 kg per 1000 kg Batteries (80 percent solids)
PbSO_4	= 0.293 kg per 1000 kg Batteries
Pb(OH)_2	= 0.140 kg per 1000 kg Batteries
water	= 20 to 65 percent

Source: Reference 5

in Section 2 of this report. The major potential sources of solid wastes associated with the manufacturing process are discussed below.

- Manufacture of positive electrode. - As noted previously, all DOE contractors have been investigating a similar process to produce the sintered plaques containing active materials (nickel hydroxide) for the positive electrode.

The sintered plaques are prepared by impregnating binder materials with nickel salts. The nickel salts are converted to nickel hydroxides in potassium hydroxide solution, and the plaques are then washed thoroughly and dried. The impregnation cycle is repeated to deposit the desired amount of active material. The plates then are sent to formation and assembly. This process will generate wastewaters and process water. The spent process water can be recycled to the process. The treatment of wastewaters will generate sludge. This sludge contains dissolved nickel and nickel salts.

The scraps generated from this process, including scrap grid, nickel powder, sintered nickel substrates, NiO electrodes, etc., can be recycled to the process of making nickel nitrate solution. Thus, no major process solid wastes are produced.

- Manufacture of negative electrode - The roll/bonding method is used to produce a negative zinc electrode. In this process, a binder is formulated with the zinc-oxide mix which is dry rolled onto a grid. A small amount of edge trim of zinc-oxide blend and grid will be generated, as are the rejected electrodes. It is not considered to be economically advantageous to separate the metal grid from the blend material. The scrap grid and electrode can be recycled, but the zinc-oxide blend would be disposed of as scrap (7).
- Battery assembly process - The major source of solid waste from this process is the sludge from treatment of wastewater. The sources of these wastes are the washing steps and accidental spills

and leaks. The quantity of the generated sludge cannot be defined since details of wastewater treatment are unknown. In a study conducted on the manufacture of a similar nickel-cadmium sintered-plate storage battery, 5.4 kg of nickel hydroxide sludge per 1000 kg of dry battery produced was reported (5). The scraps from the assembly process, such as rejected plates, grids, and batteries, are anticipated to be reclaimed.

Nickel-Iron Battery

The nickel-iron battery is similar to the nickel-zinc battery, in that both batteries use nickel hydroxide as active materials in the positive electrode and dilute potassium hydroxide as electrolytes. The only difference is the active materials in the negative electrode: one uses iron and the other uses zinc. Although the definite process for manufacturing the nickel-iron battery has not been developed by DOE's contractors, it can be assumed that the manufacturing process for this battery system would be similar to that for the nickel-zinc battery. Thus, the associated solid wastes impact should be similar to those of the nickel-zinc battery.

The major solid wastes and hazardous pollutants generated include:

- Sludges from treatment of washing water generated by the electrochemical impregnation of positive electrode; these sludges may contain nickel hydroxide and nickel nitrate salts.
- Scraps including edge trim of iron oxide and grid, and rejected grid, electrodes and others. The scraps can be disposed of in a landfill or be salvaged.

- Sludges from treatment of wastewater generated by battery assembly process. The wastewater may come from washing steps, accidental spills or leaks. The generated sludges will contain a certain amount of nickel hydroxide and iron hydroxide. The actual amounts of hazardous waste contained in the sludge will depend upon the actual manufacturing processes still to be developed, and the wastewater treatment method.

Lithium-Metal Sulfide Battery

The lithium-metal sulfide battery cell currently under development by Argonne National Laboratory and its contractors consists of FeS_2 active the material in the positive electrode, Al-Fe alloy in the negative electrode and LiCl-KCl eutectic as the electrolyte. As discussed in Section 2 of this report, ANL and its contractors have been evaluating three alternative methods for fabricating positive electrodes. These include:

- (a) Loading the active materials into the porous current collector structures made of molybdenum,
- (b) Cold-or-hot-pressing a mixture of the active material and electrolyte onto the metal current collector, and
- (c) Forming porous electrodes from a mixture of active material (FeS_2), a noncontaminating volatile material (ammonium carbonate) and a binder (graphite cement), (8).

Assembling cells in the uncharged state is currently under development. In this method, the negative electrode is a porous aluminum plaque and the positive electrode is a hot-pressed mixture of lithium sulfide, iron powder, and electrolyte. During the first charge, the lithium is transferred to the negative electrode, where the lithium-aluminum alloy is formed. In addition, ANL is also evaluating the

process for assembling cells in the charged state. The manufacturing and assembling processes for the lithium-metal sulfide battery have been discussed in detail in Section 2 of this report.

It is anticipated that a certain amount of solid waste will be generated by the manufacturing process. This may include scraps such as edge trim of plaque and electrode, residual materials, and general process wastes. There will be a high risk of explosion or fire because the wastes contain lithium or lithium compounds which react vigorously with water to release hydrogen gas and heat. The disposal or reclamation of lithium-containing solid wastes must be done extremely carefully.

3.2.3.6 Solid Wastes from Battery Disposal/Recycling

Lead Acid Battery

The approximate quantities of materials used in a typical battery with 20 Kilowatt-hour capacity (9) include:

Lead (total)	440 kg
Sulfuric acid (87 % H_2SO_4)	194 kg
Antimony	12 kg
Arsenic	0.8 kg
Calcium	0.8 kg
Case	26 kg
Total	657 kg

This battery is much heavier than a present-day lead-acid automobile battery (18 kg total weight). The added weight is more than compensated for by its high energy density.

As set forth in the preliminary performance standard document (10), the minimum life cycles of batteries are 400, and 600 cycles for near-term and advanced electric vehicles, respectively. Therefore, it can be assumed that each battery will have to be replaced at 1.3 to 2 year intervals. It is anticipated that the new battery sales will be based on a trade-in allowance for the old battery. Thus, most worn out batteries will be collected by sellers of batteries and shipped to plants for recycling. Because of the cost of the battery, it is reasonable to assume that few worn out batteries will be discarded as solid wastes.

Ideally, all the metal materials in the battery can be recycled. However, it was reported that 28 percent of battery lead was not recycled in 1969. It is anticipated that more than 90 percent of battery lead will be recycled as the recycling process improves in the future. The solid waste generation depends upon the recycling method and the materials used for battery containers and covers.

In current practice, the battery case is made of hard rubber or plastics. A mechanical method is used to recover lead from used batteries. This method first shreds both the battery cases and the internal parts, and then recovers lead in a subsequent gravity classification process. In this operation, 0.36 kg of by-product acid and 0.06 kg of by-product cases are produced for each kg of battery lead recycled. The by-product acid can be disposed of by neutralizing with some inexpensive base and discharging it as liquid waste. The sludges from the neutralization process will have potential environmental impacts because of their high concentration of toxic metals, (11).

The shredded battery cases are usually discarded as they are not useful as fuel, nor can they be easily recycled. The shredded battery cases are usually contaminated with lead and sulfuric acid, and are not biodegradable. Massive production of batteries with rubber or nonrecyclable casing for electric vehicles may result in solid waste disposal problems and undesirable environmental impacts.

The current trend in the battery industry is toward polypropylene battery casings. The polypropylene case is recyclable and can be used as fuel in lead blast furnaces. In the above mentioned mechanical process for recovering lead, the case fragments can be sent to manufacturers for recycling. Another lead recovering method subjects the battery case and the internal lead parts to intense heat and recovers the lead in a pyrolytic process. This method will generate a substantially smaller amount of solid waste in terms of furnace slag, (11).

Other Candidate Batteries

As estimated in Reference 12, the costs of the advanced batteries range from 600 to 2,930 1973 dollars. Because of the high cost, it is anticipated that virtually all worn out batteries will be salvaged or recycled. Certain amounts of solid wastes will be generated by the recycling process. As the advanced battery systems are still in the development stage, no detailed information on the procedures for recycling worn-out batteries are available at the present time. This solid waste impact assessment is qualitative and based on a material flow balance concept. A simplified block diagram indicating material flow in the battery recycling process is shown in Figure 3-15. The potential sources of solid wastes

*Solid waste source

†Potential solid waste source if non recyclable materials are used

Figure 3-15 Simplified Block Diagram of Material Flow of Used Batteries.

Source: Reference 6.

from the recycling process, as indicated in Figure 3-15, are battery containers and covers, separators, and sludge from treatment of electrolytes and washing water. These potential solid waste sources are characterized below:

Battery Containers and Covers

In the past, most lead-acid battery containers and covers were made of hard rubber. Hard rubber cases are not recyclable nor can they be used as fuel. Discarded battery cases are generally landfilled. A large scale production of electric vehicle batteries will have serious disposal problems if hard rubber containers and covers are used in those candidate batteries operated at ambient temperature.

In recent years, research on new materials, particularly plastics, for battery containers and covers has been rapidly expanding. As the minimum requirement, a battery container material (13) must be:

- Chemically unaffected by the electrolyte in the range of extreme operation temperatures,
- Rugged and rigid, but not brittle (especially) when cold,
- Reasonably compact for installation, and
- Inexpensive and easily formable.

Several existing plastics including polypropylene, high density polyethylene and others have met these requirements.

Battery containers and covers have recently become available made of polypropylene plastic. The polypropylene

container of a lead-acid battery can be sent to a smelter because it can be used as fuel in lead blast furnaces. Additionally, polypropylene containers and covers can be easily recycled. If the future electric vehicle batteries use recyclable plastic containers, the solid waste problem associated with worn-out batteries will be minimal.

There are two kinds of plastics: thermoplastics and thermosetting plastics. The thermosets, such as phenolic or ureaformaldehyde plastic, cannot be softened and reshaped through heating and, thus, are not recyclable. The thermoplastics, such as polypropylene and polyethylene can be reheated and reformed repeatedly. The use of recyclable polypropylene, high density polyethylene or other thermoplastics for the battery cases can minimize the potential solid wastes from worn-out batteries. Gould, Inc. has used a polypropylene container and cover for its experimental nickel-zinc battery (6). It is conceivable that polypropylene or other appropriate thermoplastics will be used for the near-term and advanced batteries operating at ambient temperature (advanced lead acid, nickel-zinc, nickel-iron, zinc-chlorine, zinc-bromine, zinc-air, and iron-air batteries). The solid waste impact of these batteries will be insignificant.

For the candidate batteries operated at high temperature, including sodium-sulfur and lithium-metal sulfide batteries, metal containers and covers must be used. Although the recycling process of these high temperature batteries is still unknown, it can be anticipated that the metallic containers and covers will be salvaged or recycled. The associated solid wastes should be minimal.

Separators

The separators in a used battery are saturated with electrolyte and must be discarded. Although the amount of solid waste generated will be small, used separators must be carefully disposed of.

A separator serves the dual function of isolating the electrodes electrically and retaining the particulate active material in the electrodes. Separator materials must have the proper physical properties for these dual functions. Additionally, it should be inexpensive, chemically resistant to electrolyte, long lived and easy to fabricate. Papers, fabric, microsporous plastics, inorganic/organic composite and other materials with proper physical and chemical properties may be used in the battery. At the present time, Argonne National Laboratory and its contractors are developing numerous types of separators for the candidate battery systems. The major environmental problems associated with disposing of separators saturated with electrolytes are the electrolytes. Among the electrolytes used in the various batteries, potassium hydroxide, zinc bromide, zinc chloride, and sulfuric acid, are considered as hazardous substances. (No literature has been found addressing the toxicological effects of β -alumina and LiCl-KCl eutectic). Thus, used separators should be handled and disposed of using the methods for hazardous wastes in order to minimize adverse environmental impacts.

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3.2.4 Batteries, Their Chemicals and Ecosystems

Within the life-cycles of the candidate battery systems, three steps are the major sources of environmental concern: (1) raw materials preparation; (2) storage battery manufacture; and (3) battery disposal or recycling. These are the processes where large amounts of potentially hazardous materials are handled, resulting in air and water emissions, and solid wastes. Each candidate battery system is addressed independently, and the major potential implications to the natural environment identified and discussed.

3.2.4.1 Lead-Acid Battery Systems

Several toxic agents associated with the lead-acid battery system are potential concerns. Primary and secondary smelting of lead along with storage battery manufacture are considered among the major stationary sources of environmental contamination by lead (1). Smelting also results in other emissions such as copper, zinc, cadmium, mercury, arsenic and antimony which occur along with lead in ores, as well as in emissions of sulfur oxides (2, 3). The manufacture of battery electrolyte (sulfuric acid) ancillary to the processing of direct materials releases sulfur oxides.

Lead is a well documented toxic agent (4) with no known essential function in plant or animal metabolism (5). Lead occurs naturally in living systems in small amounts, with concentrations above background resulting from anthropogenic injection into the air, water and soil system (2). Accumulation of lead in plant tissues apparently does not parallel increased concentrations in the soil. Rarsch (3) in studying vegetation

in the vicinity of a smelter, found little significant variation in lead levels among plants growing on soils having a wide range of lead concentrations. Inhalation and ingestion are the major pathways for the entry of lead into animal tissues (5) where the metal tends to accumulate in bone (90 percent of body burden) and blood, soft tissues and rapidly exchangeable bone fractions (10 percent of body burden).

The toxic effects of lead are exerted principally through the central and peripheral nervous systems, the renal system, and through enzyme inhibition (1). Placental transfer of lead has also been demonstrated, increasing the risks of lead exposure. Lead intoxication of animals tends to be seasonal, paralleling the seasonal variations in plant tissue concentrations (6). In cattle, most cases of lead poisoning are seen during the spring (plant growing season), and in the fall (2). Lead enters the aquatic ecosystem primarily through precipitation, soil erosion and leaching, lead dust fallout, municipal and industrial waste discharges, and urban runoff (7). Lead toxicity to aquatic biota varies with water chemistry parameters such as pH, hardness, organic matter, and the presence of other metals. The acute toxicity of lead is greater in soft or acid waters. Studies with fat-head minnows have resulted in 96-hour TL_m concentrations of 5.6-7.3 mg/l in soft water, versus .482 mg/l in hard water. While acute toxicity is one of the more visible effects of lead contamination, the long-term effects of sublethal concentrations can be equally important. Exposure of trout to levels as low as 0.10 gm/l has proven detrimental, while concentrations on the order of 30 mg/l has resulted in reproductive impairment of the aquatic invertebrate Daphnia magna.

Among the additional metals contained in lead smelter emissions, copper and zinc are considered essential micro-nutrients in plant and animal metabolism, although both are toxic in sufficient concentrations (8). Ratsch (3) noted that copper in plant tissues at concentrations above 20 $\mu\text{g/g}$ could result in reduced growth, stunting, and could impede the establishment of vegetation in areas containing high soil concentrations. In animals, excess copper may alter lipid metabolism resulting in circulatory disturbances such as atherosclerosis (8). Copper in the aquatic ecosystem varies in toxicity with pH, hardness, and organic content. In soft water, copper at a concentration of 60 $\mu\text{g/l}$ has been found to be toxic to trout, whereas, in hard water, 600 $\mu\text{g/l}$ was required to produce acute an equivalent level of toxicity (7).

Zinc will be addressed in detail in Section 3.2.4.3 below.

Cadmium has been found in relatively high concentrations in both soil and vegetation in the vicinity of a lead smelter (3). The metal is easily taken up by plants, especially grasses, grains and garden crops such as beets, peas, radish and lettuce. Levels on the order of 100 ng/g have been shown to reduce the growth of radishes. In animals, cadmium can result in a variety of disorders ranging from anemia, growth depression, hypertension, renal dysfunction, and other pathological processes including cancer (8). Cadmium may also cross the placental barrier into the fetal system (7). As for copper, general water quality may influence the toxicity of cadmium to aquatic life; cadmium toxicity is apparently somewhat lower when hardness is increased. (Concentrations as low as 2 $\mu\text{g/l}$ in soft water have proven lethal to species of salmonids.) Also marine organisms are able to concentrate

cadmium, posing a hazard to predators and human consumption. For example, american oysters exposed to 10 $\mu\text{g}/\text{l}$ over a five month period have accumulated up to 18,000 μg Cd/kg in whole meat.

Ratsch (3) found soil mercury concentrations in the vicinity of a lead smelter at levels classed as serious, although mercury levels in plants growing in the area did not show a direct correlation with soil concentrations. The toxicity of mercury varies greatly with the form or compound in which it occurs, (1). Monovalent mercury is generally nontoxic since Hg salts are insoluble, or only slightly so; however, the monovalent form can be oxidized to the highly toxic divalent (mercuric) form within plant tissues. Elemental mercury is toxic in the liquid and gaseous form, and organic forms of mercury are highly toxic. Choralkali plants have been noted as capable of atmospheric mercury emissions in quantities sufficient to constitute a public health hazard. Alkylmercury compounds, especially methyl-mercury, can be formed in biological systems through microbial conversion of inorganic and organic forms of mercury (9). Methylmercury, in particular, is highly toxic, subject to biomagnification through the food chain (7), and can cross the placental barrier into the fetus (1). Within the aquatic ecosystem, mercury biomagnification factors up to 10,000 fold have been demonstrated (7). Chronic exposure of fathead minnows to methylmercuric chloride at concentrations of .12 $\mu\text{g}/\text{l}$ has resulted in a complete inhibition of spawning, and while significant reproductive impairment in Daphnia magna has been noted at concentrations of 0.04 $\mu\text{g}/\text{l}$. In brief, any form of mercury is considered to constitute an environmental hazard. (7).

Arsenic occurs as a by-product in lead and copper smelting, and is toxic to some degree in most forms (1). Arsine, the gaseous form generated during smelting, is highly toxic, and can be lethal to humans in less than 30 minutes at a dose of 250 mg/kg (10). Normally less toxic than lead, arsenic may form a synergistic interaction with lead resulting in a higher toxicity at lower concentrations (1). When consumed in an organically bound form, arsenic appears to have a low toxicity (7). Ratsch found soil arsenic levels in the vicinity of a smelter at concentrations toxic to sensitive and moderately sensitive plants. In the freshwater environment, fish food organisms have been adversely affected at arsenic concentrations of 1.3 mg/l (7). Shellfish such as oysters, are also capable of concentrating arsenic.

Antimony occurs along with lead ore (2), and is utilized as an alloying agent in the manufacture of lead plates for storage batteries, although calcium is also being used for this purpose (1), and may eventually replace antimony in this application. In areas around smelters, antimony has been found to persist in surface soils, and can be taken up by animals and humans although it is uncertain if the metal is actually accumulated within organisms, and there is no evidence of biomagnification within the food chain (11). Occupational exposure to antimony (ore, metallic, and oxides) has been implicated in pneumoconiosis, and is known to result in systemic and cardiovascular disturbances. The gaseous form of antimony, stibine, attacks the circulatory and central nervous systems (12). Antimony trifluoride and pentachloride are listed as high hazard compounds by the EPA Office of Solid Waste Management Programs, and as such are

unsuitable for conventional landfill or smelting disposal methods.

Sulfur oxide emissions are associated with smelting electrolyte manufacture, and battery disposal by incineration. Ratsch (3) found sulfur enrichment of vegetation in the vicinity of a lead smelter, along with areas of vegetation injury of the types caused by sulfuric dioxide (SO_2) and acid mist. In areas of high SO_2 emissions, high levels of atmospheric sulfates and increases in water acidity have been noted. Sulfates are generally formed secondarily in the atmosphere from sulfur compounds, principally SO_2 . Sulfur dioxide has demonstrated phytotoxic properties causing injury to plant tissues not only at acute concentrations, but also with long-term exposure to sublethal levels (13). In the aquatic environment, the pH changes from sulfur emissions can alter the composition of aquatic communities. Organic sulfur compounds and inorganic sulfates can be subjected to anaerobic degradation resulting in the formation of toxic hydrogen sulfide (7). The toxicity of sulfide to aquatic biota is influenced by pH, temperature and dissolved oxygen. Sulfides are generally more toxic at lower wintertime temperatures in neutral or slightly acidic waters, and when dissolved oxygen levels are lower than normal. Pacific salmon have shown 100 percent mortality following 72 hours of exposure to 1.0 mg/l hydrogen sulfide, while reproductive impairment has been demonstrated in bluegills subjected to 1.4 $\mu\text{g/l}$ hydrogen sulfide over a 46 day period.

The electrolyte, sulfuric acid, is not only dangerous to handle, and has readily apparent effects on biota at battery concentrations, but can have toxic effects in aerosol form and in water solution. Inhalation doses of 500 mg/m^3

have been noted at the LC_{50} in rat studies (14). In aquatic studies, 42 mg/l was determined as the 48-hour TLM for mosquitofish (14), while bioassays of various marine species have resulted in toxicity levels varying from 70 mg/l for some crustaceans up to 500 mg/l for a mollusc (15).

3.2.4.2 Nickel-Iron Battery Systems

Nickel and its compounds constitute the primary environmental concern relative to this battery system. Nickel is recognized as an essential element in animal physiology although its physiological role is not established (1). Occupational exposure to airborne dust containing nickel compounds has been implicated in an incidence of sinus cancer mortality in workers two-hundred times greater than expected. Chronic effects such as blood irregularities, subatrophic and atrophic inflammatory responses of the accessory sinus cavities, and other diseases have been noted in workers subjected to long-term inhalation of nickel dust and fumes, and aerosols of nickel chlorides and sulfides. Nickel carbonyl, which is formed during the reaction between nickel and hot carbon monoxide, can result from incineration of nickel-containing wastes. Nickel carbonyl is a recognized potent carcinogen with a toxicity five times that of carbon monoxide. Other nickel compounds such as nickel carbonate, hydroxide, fluoride, and acetate have produced cancerous tumors in laboratory animals (16).

Nickel enters the food chain through ingestion and inhalation. The uptake of nickel by plants is closely correlated with the amount of exchangeable nickel in the soil, and in excess quantities can result in chlorosis (16). A concentration greater than 50 mg/g in a plant is usually toxic.

although some flowers have been found with concentrations as high as 4000 to 6000 $\mu\text{g/g}$. Animal studies have shown that ruminants apparently do not accumulate nickel beyond the levels normally found in the diet. The toxicity of nickel to aquatic life varies with the organism and parameters such as pH and the presence of other metals with which nickel may be synergistic (7). Nickel, as with lead, is apparently more toxic in soft water. Experiments with four species of fish in both hard and soft water resulted in 96-hour LC_{50} values of 4.6 to 9.8 mg/l in soft water, versus 39.2 to 42.4 mg/l in hard waters. Tests with Daphnia magna demonstrated significant reproductive impairment at concentrations as low as 30 $\mu\text{g/l}$ in soft water. Nickel may be subject to biomagnification through the food chain (16). Marine plankton and brown algae have shown concentration factors of 1700 and 140 to 500, respectively, above environmental background.

Iron and its compounds are of most concern relative to the aquatic environment. Iron is an essential trace element to plants, serving as a limiting factor in growth, and to animals where it is essential to oxygen transport in the blood of all vertebrates and some invertebrates. In waters devoid of dissolved oxygen, soluble ferrous iron can persist in the deep anaerobic waters of lakes until the autumn or vernal turnovers reintroduce oxygen into the system, resulting in the precipitation of iron as ferric hydroxide (7).

The precipitation of ferric hydroxide occurs as a gel or floc, and in sufficient quantities can result in the smothering of benthic invertebrates, plants, fish eggs, and render spawning beds unusable. In some situations, the hydroxide floc can solidify the lake bottom or stream bed, completely destroying its value as habitat. Ferric hydroxide precipitate (known as "yellow boy") is generally associated with

industrial wastes and mine drainage, and can result from iron-bearing groundwater entering a lake or stream. Iron at concentrations as low as 1.8 mg/l can affect the taste of water; and at high concentrations, can stain clothes and plumbing fixtures. Iron is known to be toxic to aquatic biota with factors such as pH, alkalinity, hardness, temperature and ligands altering the toxicity. Mayflies, stoneflies and caddisflies have recorded 96-hour LC_{50} values of 0.32 mg/l, while pike and trout have succumbed at concentrations of 1 to 2 mg/l. Studies of a Colorado stream have revealed a total lack of fish life in areas containing iron at concentrations above 1 mg/l. In alkaline sea water, dissolved iron can precipitate, posing a possible hazard to benthic dwellers such as shellfish.

Potassium hydroxide, the electrolyte used in this and other candidate battery systems, is a dangerous substance in the concentrated form, causing severe burns. Entry of battery electrolyte into the aquatic environment in sufficient quantities could result in substantial pH change, leading to mortality of aquatic biota in the affected area. In even smaller quantities, potassium hydroxide can be toxic to aquatic life. Studies with mosquitofish have resulted in acute toxicity within 24 to 96 hours at concentrations of 80 to 85 mg/l, while trout have succumbed within 24 hours at concentrations of 50 mg/l (17). Potassium hydroxide at concentrations of 150 to 500 mg/l have proven lethal to snails.

The manufacture of potassium hydroxide by the Diaphragm Cell and Mercury Chlor-Alkali processes results in a variety of toxic by-products such as asbestos (Diaphragm Cell), chlorinated hydrocarbons (both processes), and mercury (Mercury Chlor-Alkali). Mercury was addressed in Section 3.2.4.1

above. Asbestos is toxic through inhalation, and possibly by ingestion (18). Inhalation of asbestos-laden dust by workers can result in asbestiosis, a "dust lung" disease, even years after exposure has ceased. Asbestos has also been shown to increase the risk of lung cancer. The toxicity of asbestos through ingestion is not clearly established. Chlorinated hydrocarbons consist of numerous compounds, including chloroform and carbon tetrachloride formed during the production of chlorine by the Diaphragm Cell process. This group of compounds is highly toxic even in very small amounts that produce little or no indication of overt intoxication. The calculated safe levels for exposure of man ranges as low as 0.0003 mg/kg/day for certain chlorinated hydrocarbons (18). Aquatic biota are also highly susceptible to this family of compounds with toxic levels recorded in fractions of a part per billion (7).

3.2.4.3 Nickel-Zinc Battery Systems

The nickel compounds, potassium hydroxide electrolyte, and the major toxic by-products associated with electrolyte manufacture have been addressed in Section 3.2.4.2 above. Sulfur oxides, a product of the smelting of zinc and other metals, was addressed in Section 3.2.4.2.

Zinc is an essential element in both plant and animal nutrition. It is necessary to the function of several enzymes, particularly in protein synthesis (19). Atmospheric zinc is derived primarily from zinc, lead and copper smelting, galvanizing, and from secondary processing such as scrap recovery (1). Human exposure to zinc can result in generally non-fatal "metal fume fever" through the inhalation of zinc oxide which is produced when zinc is heated. "Metal fume

fever" generally does not occur at exposure levels of 15 mg/m³ or less. Zinc oxide exposure at concentrations of 400 to 600 mg/m³ have resulted in liver and lung damage in rats, with death in 10 percent of the cases (1). Zinc chloride fumes are moderately toxic, although fatalities have resulted from inhalation of high concentrations. Nonoccupational exposure of humans generally occurs through food consumption, especially protein-rich foods such as meats and marine organisms, (oysters are particularly high in zinc content, 19). Zinc levels of 10 to 100 mg/kg are normally found in plants such as most crops and pasture plants. Zinc is generally not toxic to plants unless an emissions source is near. Ratsch (3) found no evidence of zinc toxicity in plants growing near a lead smelter, although soil concentrations reached 300 µg/g. Studies with rabbits, dogs and cats have shown sublethal effects such as a fall in body temperature, leukocytosis, and increased pulmonary air flow resistance with inhalation exposures to zinc oxide at 100 to 600 mg/m³, and zinc sulfate and zinc ammonium sulfate at 1 to 2 mg/m³ (19). Reports have indicated that dietary exposure of rats to 150 mg zinc/kg, was harmful to the fetus. There is no evidence to date that zinc is carcinogenic. Zinc tends to occur with cadmium, which is highly toxic, as an impurity. Cadmium was addressed earlier in Section 3.2.4.2.

The toxicity of zinc in the aquatic environment is modified by factors such as hardness, dissolved oxygen, temperature, and the presence of alkaline earth metals which are antagonists to the action of zinc salts (7). In soft water, zinc is synergistic in toxicity with heavy metals such as copper. The toxicity of zinc is increased by a rise in water temperature or a reduction in dissolved oxygen. In soft water, the LC₅₀ of zinc to fathead minnows was recorded at

870 µg/l, while in hard water the LC₅₀ rose to 33,00 µg/l. Chronic exposure of fathead minnows to 180 µg/l in hard water, resulted in an 83 percent reduction in egg production, while significant reproductive impairment in Daphnia magna resulted from chronic exposure to zinc at 70 µg/l in soft water. Zinc is accumulated by some marine species, with tissue levels up to 1500 mg/kg recorded. The primary impact of zinc compounds will be felt by the aquatic environment acting as a receiving body for processing wastes from various stages in the battery life cycle.

3.2.4.4 Iron-Air Battery Systems

The toxic agents of primary concern, iron and its compounds, and the electrolyte potassium hydroxide, were addressed earlier in Section 3.2.4.2 above.

3.2.4.5 Zinc-Chlorine Battery Systems

The major toxic products associated with this sytem have been addressed earlier: zinc and its compounds in Section 3.2.4.3; sulfur oxides from smelting in Section 3.2.4.2; and hazardous substances from chlorine manufacture such as mercury (Section 3.2.4.1) and chlorinated hydrocarbons (Section 3.2.4.2). Two additional toxic agents associated with this battery system, chlorine and titanium, will be addressed here.

Chlorine is a highly toxic gas in its elemental state, and is highly water soluble. The toxicity of chlorine gas to plant and animal life is exerted through its denaturing effect on tissues (7). In water solution, chlorine is acutely toxic to aquatic life in various ways, including pH alteration, direct action of the hydrolysis product HOCl (which is also bactericidal in action), and through the formation of chloramines (combined available chlorine) from the reaction of free available chlorine (HOCl and OCl) with nitrogenous organic materials in water. The toxicity of chlorine to aquatic life is generally regarded as a function of the total residual chlorine in the water, (free available chlorine plus combined available chlorine). Residual chlorine has been found instrumental in effecting a reduction in the number of fish species downstream of chlorinated wastewater discharges, where no fish were found in areas where residual chlorine concentrations reached 0.37 mg/l. Studies have shown that "cold water" fish such as trout and salmon are highly susceptible to residual chlorine with lethal levels recorded in the range of 0.006 to 0.08 mg/l. "Warm water" species such as perch and bass have proven susceptible at concentrations of 0.09 to 0.30 mg/l residual chlorine. Marine biota are also sensitive to residual chlorine. Phytoplankton primary productivity has been substantially reduced with continuous exposure to 0.10 mg/l, and oysters have reacted adversely to 0.05 mg/l through a decreased pumping rate, with pumping ceasing at 1.0 mg/l residual chlorine.

Titanium may be utilized in this battery system for electrode support, and may also appear in the nickel-zinc and nickel-iron battery systems but in lesser amounts. There is currently no evidence that titanium serves any metabolic function in life systems (20). Available data indicate that

titanium has a low toxicity to plants and animals, being only little absorbed through inhalation or ingestion. The most commonly used forms are metallic titanium and the oxide, both of which have shown low toxicities in animal studies. Other forms of titanium such as the carbide, nitride and hydride resulted in heart, liver and kidney damage in experimental animals. Soluble titanate has disturbed reproductive processes with teratogenic effects in animal studies, and some organic compounds such as titanocene have shown carcinogenicity. Some salts of titanium have reportedly caused mutagenic effects in plant studies.

3.2.4.6 Zinc-Bromine Battery Systems

Little information exists relative to this battery system. The hazardous agents associated with zinc production have been addressed above: zinc in Section 3.2.4.3; sulfur oxides from smelting in Section 3.2.4.1; and other possible toxins such as mercury from smelting and electrolyte manufacture in Section 3.2.4.1; chlorinated hydrocarbons from electrolyte manufacture in Section 3.2.4.2, and chlorine and titanium in Section 3.2.4.5.

Bromine gas is extremely hazardous to both terrestrial and aquatic life. Toxic effects have been noted in man with inhalation exposure to bromine gas at 40 $\mu\text{g/g}$ (15). In the aquatic environment, bromine in solution has proven lethal to algae at concentrations greater to 0.42 mg/l with substantial mortality seen at concentrations 0.018 mg/l (17). Fish have succumbed within 15 to 96 hours at levels of 20 mg/l, while 10 mg/l has proven lethal to Daphnia magna.

3.2.4.7 Sodium-Sulfur Battery Systems

Little data exists relative to this battery system. The toxic effects of sulfur oxides, in this case resulting from sulfur production and battery fires, have been addressed in Section 3.2.4.1. Chlorine, which is a co-product with sodium in the Down Cell process has been addressed in Section 3.2.4.5. Sodium metal is well known as a highly reactive and hazardous metal in the presence of water. Entry of a large amount of unprotected sodium metal into an aquatic environment would result in the obvious explosive effects, and could also adversely affect aquatic biota not residing in the immediate area, through a rapid temperature increase which could be lethal to sensitive species, or via a sudden increase in pH from the formation of sodium hydroxide. The hydroxide of sodium has been shown toxic to a variety of aquatic species with acutely lethal concentrations reported from 1.0 mg/l for some fish eggs and fry, to 240 mg/l for Daphnia magna (17). Other sodium compounds have shown lower toxicities such as the sulfate where acute toxicities have been reported at 320 mg/l for aquatic insects, to as high as 14000 mg/l for some fish. The sulfide of sodium is more toxic with lethal levels reported as low as 0.55 mg/l for juvenile carp, to as high as 1000 mg/l for freshwater oligochaetes.

3.2.4.8 Lithium-Metal Sulfide Battery Systems

Very little documentation exists regarding toxic products associated with this system. Sulfur oxides, which could result from a battery fire, have been addressed in Section 3.2.4.1. The toxic properties of lithium and lithium salts such as the chloride are poorly documented. Lithium metal is explosive in reaction with water, while lithium chloride was

once used as a table salt substitute, resulting in severe toxic effects to humans causing death in some cases (21). Lithium is found in biological materials only as a trace, and there is no evidence that lithium is essential to any physiological processes (22). Lithium is also reported to influence a number of enzyme systems. The pharmacological uses of lithium compounds have been established, and are used in drug therapy. Lithium affects the central nervous system, sometimes resulting in irreversible brain damage and renal failure (23). Lithium chloride has been associated with cardiovascular failure.

Iron and its compounds were addressed in Section 3.2.4.2. Iron sulfide, in the aquatic ecosystem, results in the formation of black mineral muds (7); although little is known of the toxic effects of this compound.

Potassium chloride, a component of the eutectic salt mixture along with lithium chloride, is not well documented in the toxicity literature. In the aquatic environment, studies with fish and invertebrates have yielded toxicities at concentrations ranging from 940 ppm to 2010 ppm (15).

3.2.4.9 Lithium-H₂O-Air Battery Systems

Lithium and its compounds were addressed in Section 3.2.4.8.

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Appendix A: Li/MS Battery Description

Lithium-Iron Sulfide Battery

The lithium-iron sulfide battery is in the research and development stage. Two complementary efforts are underway at Argonne National Laboratory (ANL) that are directed to the development of lithium-metal sulfide cells and batteries for use in propelling electric vehicles. One effort is a design study in which specifications for these cells and batteries are being developed; in the second, tests are being conducted to determine the performance of present-day engineering-size cells. Both cylindrical and prismatic geometry cells have been developed with negative electrodes of a solid lithium-aluminum alloy (~50% Li) and positive electrodes of iron sulfide (FeS_2). The electrolyte is molten salt LiCl-KCl which required an operating temperature of 400-450°C.

The results of one cell and battery design study (1) provide the specifications given in Table A-1. The battery design consists of 10 hermetically sealed modules with each module containing eleven Li-Al/ FeS_2 cells. In this module, the cell housings are insulated from each other and from the module jacket. The module jacket, which is a hermetically sealed stainless steel container, provides additional protection to the cells from the atmosphere. A voltage lead from each individual cell is connected to a multiple conductor feedthrough in the wall of the module jacket. The conceptual battery design is shown in Figure A-1.

The battery is insulated with a vacuum jacket containing multifoil insulation. This insulation, with allowance for heat losses through the battery terminals, would meet the

Table A-1. Design Specifications for Optimized Multiple Cells.

Design Specification	Li-Al/FeS ₂
<u>Cell</u>	
Number of Cells/Battery	100
Diameter, cm	15.0
Height, cm	4.63
Average Voltage, V	1.30
Theoretical Capacity, A-hr	392
% Utilization at End of Discharge	75
Energy Output, W-hr	382
Specific Energy, W-hr/kg	173
<u>Component Weights, g</u>	
Li-Al	497
FeS or FeS ₂	435
Separator	53
LiCl-KCl	691
Housing	217
Current Collector	218
Plate Hardware	20
Feedthrough	75
Total Weight	2206
<u>Power and Specific Power</u>	
Peak, W	546
W/kg	248
Normal, W	164
W/kg	74
<u>Current and Current Density</u>	
Peak, A	420
A/cm ²	0.430
Normal, A	126
A/cm ²	0.129

Source: Reference 1

Figure A-1. Conceptual Battery for Electric Vehicle Propulsion.

Source: Reference 2

Figure A-2. Li-Al/FeS₂ Engineering Test Cell.

requirements of 150 to 200 W heat loss. Heater tapes are provided for battery start-up and for maintaining battery operating temperature during extended periods of vehicle inactivity. When the car is operated continuously for more than half an hour of highway driving, the temperature in the battery will build up as a result of heat generation from resistance and diffusion losses within the battery. Both liquid cooling and air cooling were considered for removal of this heat. It was concluded that air cooling would be the less expensive and more efficient method. The air flow is provided by a scoop under the car, since only 15 to 20 cfm airflow is required. The incoming air is heated by countercurrent heat exchange within the battery pack before it comes in direct contact with the battery modules. This heated air can be used to heat the car interior during winter months.

A schematic diagram of the type of cells that have been developed and tested in the DOE program is shown in Figure A-2. The iron housing is 13 cm in diameter and 4 cm high. The cell contains two negative electrodes (Li-Al) and one positive electrode (FeS_2). The active material in the positive electrode is contained in a stainless steel screen enclosure that is in direct contact with the negative electrodes. A separator of boron nitride (BN) fabric and a particle retainer of zirconia fabric are inside the steel screen enclosure. Overlap of the separator cloths prevents active material from shorting to the screen support. The positive electrode current collector consists of three molybdenum screens welded to a molybdenum hub and a molybdenum current lead.

ANL efforts in electrode and cell development have resulted in the identification of designs for electrodes and cells and new procedures for cell assembly and start-up.

Several promising types of positive electrodes have been designed for prismatic cells; these include:

1. electrodes having porous current collector structures into which the active material is vibratorily loaded;
2. electrodes in which a mixture of the active material and electrolyte is hot-pressed onto a metal current collector; and
3. electrodes formed from a mixture of active material and carbon cement to give a carbon-bonded, porous structure that is easily penetrated by electrolyte.

Alternative materials for the separators are being investigated by ANL. Boron nitride fabric has shown adequate performance as an electrode separator in engineering cells; however, a lower cost, thinner separator of improved performance is needed for commercial batteries. Advanced concepts include BN paper having a BN binder formed by nitriding B_2O_3 binder. Separators consisting of BN fibers and ceramic powders (BN, MgO , $LiAlO_2$) with a small (<4%) addition of asbestos fiber as a binder are also being evaluated. Separators with combinations of fibers (Y_2O_3 , BN) and ceramic powders (Y_2O_3 , AlN) are also being investigated.

ANL has contracted with several manufacturers of ceramics for the development of electrical feedthroughs. The 3-M Corp., Chattanooga, Tennessee, has applied nickel and gold platings to the braze zone of beryllia feedthroughs that were metallized by standard methods. ILC Technology, Sunnydale, California, is developing niobium-base brazes for beryllia and is producing prototype feedthroughs for in-cell testing. Coors Porcelain Co., Golden, Colorado, is producing yttria bodies and will metallize them with an oxide-base braze to form feedthroughs. Ceramaseal Inc., New Lebanon Center, New York, has developed

a mechanical-type feedthrough, in which the seal is formed by forcing a beryllia body into a high-strength steel tube. Samples of the various feedthroughs are being procured for evaluation.

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