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An accounting of the materials flows for lithium

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1.0 Introduction

Lithium provides hope for the future of batteries. Its unique chemical capabilities make it an excellent candidate for high power low weight batteries. However, before wide scale use of lithium is established in the industry, a study should be undertaken to see if there are any major possible side effects of lithium, and if so what are the possible risks to humans should lithium use be increased as expected. One approach to this problem is a large scale material balance for lithium.

1.0.1 Materials Accounting

Materials balance has been around since the beginnings of engineering. It is based on the simple principle that whatever comes in must go out. Yet, applying the material balance principles to such a large scale has been a relatively new idea. By applying the material balance principle to the United States, we can track the materials flows of certain elements. By seeing how recycling is accomplished and how the industry uses the material in question, a precise picture of material flows can be assembled. This knowledge includes how much of the chemical is exposed to human beings. Coupling data on how much of a particular material is in humans with health studies can help shape public policy on the issue of lithium. An advantage of the material balance approach is that future trends of the material can be predicted. One can try to estimate the relationship of environmental discharges to total material throughput. Despite material balance's simplicity, it suffers from a lack of data, which makes the material balance subject to large errors.

1.0.2 Why Lithium?

Lithium is of interest because its use in industry is growing. It has potentially serious environmental impacts, as high doses have been shown to be lethal to humans. With potential serious health effects, knowledge of how much lithium is exposed to humans is vital. The following table shows the amount of per capita consumption of lithium and various other metals for comparison.

Per Capita Annual Consumption of Various Metals in 1994

Metal	Consumption (g)
Al	29200
Cu	11200
Pb	6000
Zn	5400
Cr	1548
Ni	642
Sb	180
W	33.6
Li	9.2
Cd	**8.08**
Hg	**2.2**
Se	**1.84**

(19)

1.1 Properties of Lithium

Lithium is an extremely reactive metal when found pure; it is never found in nature as free metal. It is typically found in an ionic compound, usually the oxide. Some important properties of lithium follow:

Properties of Lithium

Atomic Weight	6.491
Melting Point	180.5 °C
Boiling Point	1336 °C
First Ionization Potential	519 kJ/mol
Electron Affinity	52.3 kJ/mol
Crystal Structure	Body Centered Cubic
Density	0.531 g/cm^3
Specific Heat at 25°C	3.55 J/g
Heat of Fusion	431.8 J/g
Heat of Vaporization	21.3 kJ/g
Electrical Resistivity	9.446 jift-cm^3
Standard Oxidation Potential	+3.045 V

(1)

Some of these properties are quite interesting. First, the oxidation potential of lithium is the highest of any metal. This property makes it an excellent candidate for battery manufacture as each electron given up by lithium will produce the more energy than any other element. Also, the atomic weight of lithium is the lightest among the elements, which means lithium could have applications in low weight applications. Lithium's density is also quite low, lower than water's, which implies that lithium artifacts could be light and float on water.

2.0 Sources of Lithium

The first consideration in the mass balance of lithium is natural sources. Lithium is so scarce in the earth, that it could be considered a rare earth element. The average concentration of lithium in the earth's crust is less than 20 parts per million (2). Despite its minuscule concentrations, it is feasible to obtain lithium in the pure form. This is accomplished from two sources mainly. The first source is lithium rich ores, including spodumene (LiAlSi2O6), lepidolite (K(Li, Al)3(Si, Al)40io(F,OH)2), and petalite (LiAlSi4Oi0).

Spodumene is the main source of lithium from ore. The other major source of lithium is salt brines. Some naturally occurring salt brines contain up to 1000 parts per million lithium, which can be concentrated to produce lithium. Economic reserves of lithium include the North Carolina spodumene mines and the brine lakes of Nevada, Chile, and Bolivia. Lithium reserves worldwide are quite large, in proportion to lithium's current usage. This is especially true if one considers that the world's oceans contains 170 parts per billion lithium. Estimated economical reserves as of 1980, as reported by the US Geological survey, are 1.1 million tons ultimate with 0.6 million tons remaining. According to the US Geological Survey, these reserves should be adequate to provide well into the 21st century. (2)

2.1 Producers of Lithium

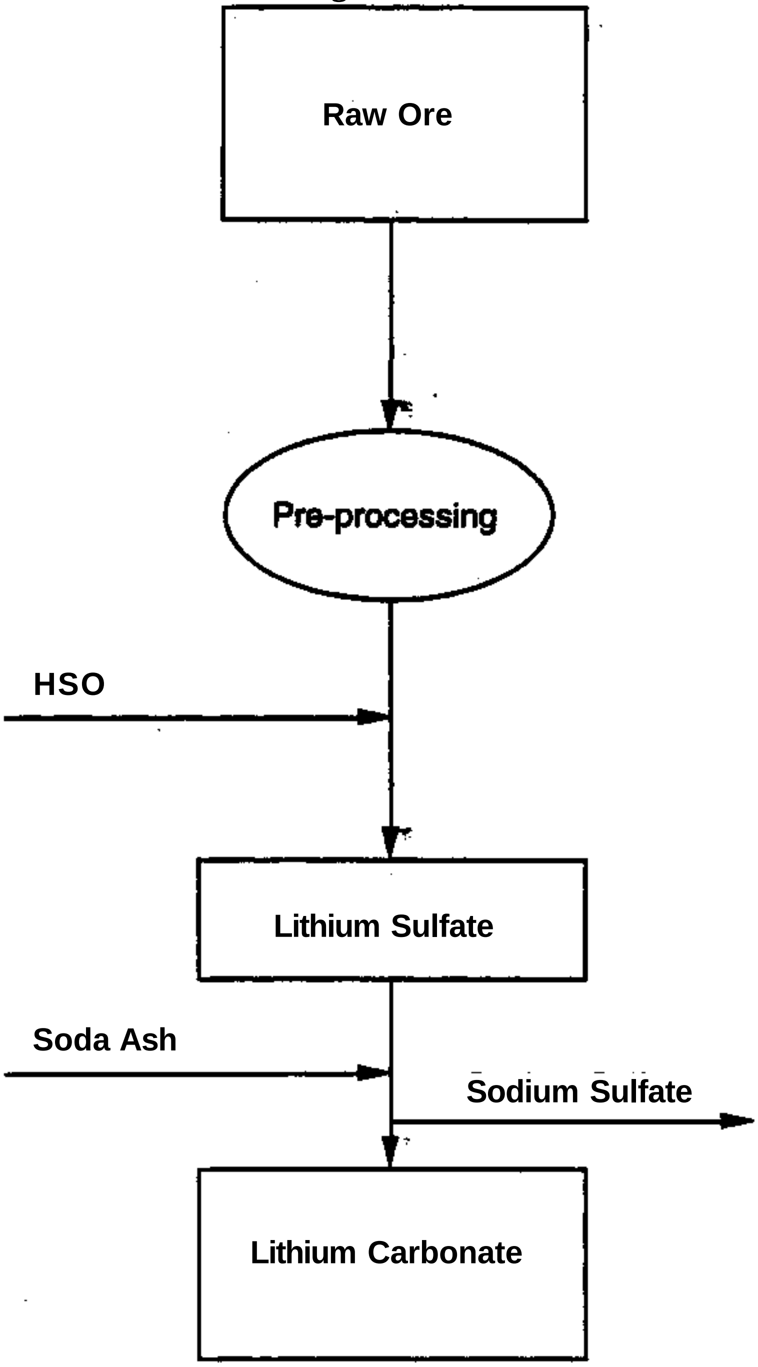
Two major domestic companies account for all US production, Cyprus Amax Minerals Company and FMC Corporation. (3) Cyprus Amax operates a profitable lithium business, making $23 million from their lithium business in 1994. Cyprus Amax tauts itself as "the world's largest and lowest-cost producer of lithium carbonate" (4). Cyprus made 32 million pounds of lithium carbonate equivalents in 1994. Cyprus Amax plans on expanding their lithium business in response to expected increase of demand in such sectors as the aluminum industry and glass industry. Cyprus wants to expand into a new brine production facility in Chile, and expand their downstream product production. No information is available from FMC Corporation. (4)

3.0 Processing of Lithium

Lithium ore itself has very few uses; it must be refined into another product, usually lithium carbonate. It is preferred to ore because it is more reactive than the lithium oxide found in the ore. It is relatively easy to refine further and to transport easily. In order to produce lithium carbonate, the ore must first be heated up to high temperatures, in order to react it with sulfuric acid, which converts the lithium in the ore into lithium sulfate. This mixture is then washed and separated. Then, the lithium sulfate is reacted with sodium carbonate, precipitating lithium carbonate. This lithium carbonate mud is washed and purified. The lithium carbonate is then processed for customer needs. (5)

Purification from brine produces lithium carbonate as well but the process differs from that from ore. The brine process involves the collection of the brine into huge drying ponds. This concentrates the lithium as other salts, like sodium and magnesium, precipitate. The lithium rich brine is then precipitated with sodium carbonate. This is washed and collected for other uses. (3)

A Schematic Flow Diagram for Lithium Processing



(3)

The lithium is then processed into lithium carbonate. This lithium carbonate is then further refined into butyllithium, lithium metal, lithium hydroxide, and lithium bromide for the various end uses which are described in section 5. After purification lithium carbonate is changed into other products for use in other industries. Lithium carbonate is used itself in some industries, namely the aluminum and glass industries. Lithium carbonate is also fed to other processes to make other compounds. One of these compounds is lithium hydroxide.

$$Li_2CO_3 + H_20 \longrightarrow HCO_3\text{- -h } Li\text{+ -K } LiOH$$

This compound is usually produced as the monohydrate. This compound is used in further lithium processing and in the air quality control industry. Lithium hydroxide is converted to lithium chloride by treating the hydroxide with hydrochloric acid.

$$LiOH + HC1 \longrightarrow LiCl + H2O + energy$$

Lithium chloride itself is not a major lithium product, but it is used to make pure lithium metal. This is done through a electrolytic process. The lithium chloride is split into free lithium and chlorine gas.

$$2\ LiCl + energy \longrightarrow 2\ Li(s) + Cl_2\ (g)$$

The chlorine gas is collected and used in other processes. The molten lithium metal is collected and cooled as well. Lithium metal is used as a catalyst in some applications and is also used in the production of lithium batteries. Another important organic reagent is made from lithium metal. Butyllithium is produced by the reaction of lithium metal with chlorobutane.

2Li(s) + /X/^Q——————* /\S* Li + LiC1

Butyllithium is used in several polymerization reactions, in addition to other reactions. Each of these products tends to be quite expensive, as could be expected by the high energy requirements to obtain lithium from ore. The following table shows average price of lithium in 1994.

Lithium Prices, 1994

Lithium Products	Dollars per pound
Lithium Bromide	5.67
Lithium Carbonate	2.00
Lithium Chloride, anhy	4.84
Lithium Fluoride	7.14
Lithium metal ingots	35.98
Lithium Sulfate, anhy	4.45
Lithium hydroxide monohydrate	2.55
n-Butyllithium (15%) in hexane	20.20

(3)

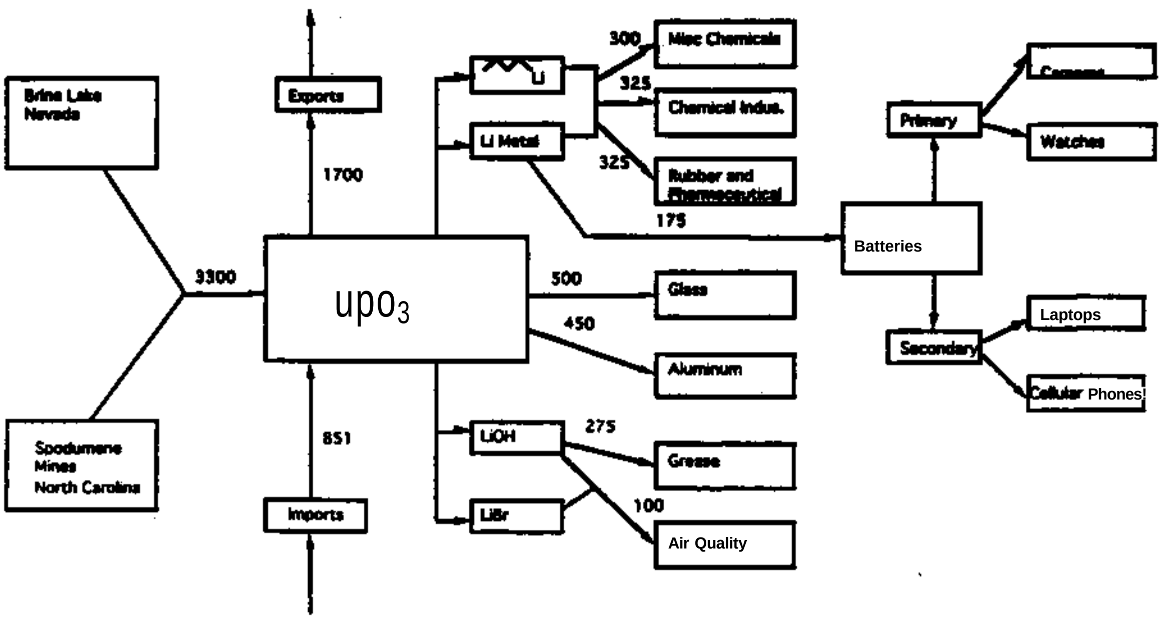
4.0 Materials Balance for Lithium

The materials flow balance for lithium is fairly complete qualitatively, but quantitatively many exact numbers are missing. This is due in part to some company proprietary data, and some lack of knowledge as to what is happening to the lithium. The lithium is obtained from three sources, Nevada, North Carolina, and imports. The lithium is then processed into lithium carbonate and other lithium products for use in various industries. The largest user of lithium is the glass industry taking in about 20% of the annual consumption of lithium. Next is the aluminum industry and the chemical industry. These three groups account for more than 50% of the lithium consumption. The other industries are represented on the diagram as shown. The lithium flow diagram ends with the end uses because no accounting of recycling or waste management has been discovered. The available qualitative data suggests that the lithium is leaked into the environment, due to the lack of recycling information and specific data on the processes which is discussed in sections 5 and 7.

Quantity of Lithium Used Per Industry

Industry	Percent Lithium Used
Glass	20%
Aluminum	18%
Rubber and Pharmaceuticals	13%
Chemical Industry	13%
Miscellaneous Chemicals	12%
Lubricants	11%
Batteries	7%
Air Quality	4%

A Material Flow Sheet for Lithium - 1994 United States



Data in Metric tons of contained lithium

Lithium Statistics
(Metric tons of contained lithium)

	1990	1991	1992	1993	1994
Imports	790	590	770	810	851
Exports	2600	2400	2100	1700	1700
Estimated Consumption	2700	2600	2300	2300	2500
Estimated Production	4510	4410	3630	3190	3349

(3)

5.0 Use

Understanding the uses of lithium is critical to determining the possibilities of release into the environment and potential sinks of lithium.

5.1 Glass

The glass industry uses lithium in several of their products to enhance performance of the glass. Lithium is added to glass to make the glass more heat resistant, by lowering the coefficient of thermal expansion. A precise amount of lithium carbonate is added to certain glass and ceramics to make various products. Lithium glass goes by certain trade names. Different compositions of lithium in glass are denoted by various trade names, such as Corningware™, a popular cooking material. Lithium in the glass makes Corningware™ more resistant to thermal expansion and cracking. (2,5)

Data on possible recycling of lithium glass is missing, but the available data suggests that little recycling is done of lithium glass.

Composition of Various Glasses Containing Lithium

Oxide	Fotoform	Enstatite	Pyroceram
SiO2	79.6%	58.0%	67.3%
Li2O	9.3%	0.9%	0.8%
MgO		25.0%	14.3%
AI2O3	4.0%	5.4%	1.8%
Na2O	1.6%		3.0%
K2O	4.1%		4.8%
GO			4v7%
BaO			0.3%
F			3.5%
P2O5			1.0%

(5)

5.2 **Aluminum Industry**

Another major use is the aluminum industry. The aluminum industry uses lithium carbonate as an additive to the Hall-Heroult cell electrolyte, which is cryolite (NaAlF4>. The lithium carbonate reacts in the electrolyte to make lithium fluoride, by the following reaction.

$$2\ AlF3 + Li_2CO_3 \longrightarrow 6\ LiF + Al2O3 + 3\ CO_2$$

This lithium fluoride combines with the electrolyte to lower the melting point of the electrolyte, allowing a lower operating temperature, an increase in conductivity, and a lower solubility of aluminum in the electrolyte. (6) These effects are summarized below.

Variations Induced by Additives to Cryolite

	Solidification Temperature CO	Electrical Conductivity	Density Variation (g/cm^3)	Interfacial Tension	AI2O3 Dissolution Rate
Cryolite	**0**	**0**	0	**0**	**0**
+3% NaF	**-2**	**+0.03**	+0.01	**-**	**+3**
+3%UF	**-23**	**+0.13**	-0.01	**+40**	**-7**
+39&KF	**-20**	**-**	**-0.01**	**+30**	**-**
+3% BeF2	**-25**	**-0.15**	**-0.03**	**+90**	**-**
+3% MgF2	**-12**	**-0.22**	**+0.01**	**+60**	**-9**
+3% CaF2	**-7**	**-0.11**	**+0.02**	**+20**	**-6**
+3% BaF2	**-3**	**-0.09**	**-**	**0**	**-**

(20)

All of these lead to a higher yield of aluminum per energy expended. Throughout the life of the cell, it is likely that the lithium fluoride is caked on the sides of the cell wall. After the cell has completed its economic life, it is cleaned and an attempt to recycle the fluoride is made. Potentially, all of the lithium may be recovered, noting lithium's high cost. The recycling process involves the cleaning of the spent cells with sodium hydroxide to dissolve the fluoride salts, filtration of this liquor, and adjustment of the mixture to prepare for recycle back into fresh cells. It is possible that the lithium is filtered out with the filtration. Adjustments to this process could be made to allow for a higher recovery of lithium from this liquor. (7)

Exact process description of the lithium in the electrolytic cell is missing, as well as possible recycling efforts. However, current knowledge of the recycling of spent cells suggests that little recycling is done.

5.3 Chemical Industry

Another important use is the chemical industry. Butyllithium is used as a catalyst in the production of synthetic rubber, polystyrene or polybutadiene. (8) The butyllithium undergoes an attack on the double bond system of the styrene or butadiene. This results in an anionic species which undergoes further attack on more butadiene or styrene molecules. In this reaction, the butyllithium acts as a chain initiator. (9) One interesting aspect of the catalysis of polymerization with butyllithium is that the styrene or butadiene polymerizes in a narrow molecular weight range. This allows for engineering of the rate of addition of feed and catalyst to the reaction mixture to obtain products of any desired molecular weight range. Also, the polymers catalyzed by lithium tend to have little or no branching. Branching is an effect where the catalyst begins a new chain on the polymer itself. This creates a spread out polymer instead of a straight polymer. Some applications of polymers require straight chains and others require highly branched polymers. In either case, the quantity of branching must be controlled. Lithium catalysts can help control branching in the reactor vessel. The end product of the initiation of polymers by lithium is lithium chloride. The chances of any recycling attempt of this lithium chloride are small.

Lithium metal could also be used as a reducing agent, owing to its tendency to give up electrons. More than likely, the chemical industry uses lithium metal in this capacity as well.

Again, data on the chemical industry is lacking, such as the exact uses and amounts of lithium in certain chemical processes, the extent of recycling of lithium, and the ultimate fate of lithium. Finding out information on how much lithium each company uses is difficult, as this type of data is likely considered proprietary.

5.4 Pharmaceutical Industry

Much like the chemical industry, the pharmaceutical industry likely uses lithium as a catalyst in the production of several drugs. However, in addition to its use as a catalyst, lithium is also administered to patients to control manic-depressive mood swings. This use was discovered by John Cade, an Australian in his experiments on guinea pigs during the 1940's. He discovered that the guinea pigs were very docile after injections of lithium urea. He thought this could be a breakthrough so he began testing on himself and his patients. From then on lithium has been given to manic-depressives worldwide for the treatment of their moods. However, patients on lithium must be monitored carefully as an overdose of lithium is potentially fatal. Reactions to lithium vary widely by person and concentration of lithium. Care must be taken to ensure that the proper dose of lithium is being received. High doses of lithium can be deadly. (10)

Which drugs lithium is used to produce, how much lithium is used for each product, and if any recycling is performed is not known. Data such as this might be difficult to find due to the fact that much of this type of data is considered proprietary.

5.5 **Grease**

Lithium is also employed in the manufacture of certain greases. Lithium hydroxide is reacted with the appropriate fats, typically those found in animal fats, oleic, stearic, lauric acids, creating lithium carboxylates. These lithium carboxylates are then added to petroleum products to thicken the grease. Lithium carboxylates have excellent properties like heat resistance, water resistance, and mechanical stability. (11)

Very little is known about how lithium in grease is actually used, much less any recycling efforts. All that is known is that lithium is used in this manner and a basic idea of how it is used.

5.6 Air Quality

In the air quality business, lithium has two distinct uses. First, a lithium bromide-water solution is used as an absorbent in refrigerant systems. This system has the excellent properties of easy separation of the refrigerant and absorbent and strong affinity for the refrigerant at the appropriate temperature and pressure ranges. However, lithium bromide and water crystallizes at low temperatures, thus limiting its usage in low temperature applications.

Another use of lithium is in closed systems, like submarines. Lithium hydroxide absorbs carbon dioxide out of the air thus regenerating the air for further use. (2,12)

The use of lithium in the air quality industry is known on a very general level. A deeper understanding of the absorbent and the air regeneration process is lacking. It is not known at this time how the lithium is disposed of after use or how the lithium could potentially leak during use.

5.7 **Batteries**

The use of lithium in batteries potentially represents one of the fastest growing areas of lithium use. Batteries are divided into two main types: primary and secondary. Primary batteries are batteries which cannot be recharged and are used once and thrown away.

Secondary batteries are designed to be recharged and used again and again. Lithium batteries have several advantages over other types of batteries. First, lithium batteries have a higher power mass density than other types of batteries on the market currently. Power mass density is defined as power of the battery divided by its weight, including packaging, electrolyte, etc. This low weight is due to lithium's low atomic weight. Another advantage of lithium batteries is their high power volumetric density. This property is due to lithium's high oxidization potential. These two properties make lithium batteries a hope for the future. (13)

The use of lithium in primary cells is well established. Lithium-manganese dioxide batteries are used in watches and cameras and are well-suited for these purposes because they do not deplete appreciably over time. Some lithium batteries in watches last several years at least. For the same reason, lithium batteries are also used as backup batteries in computers. (14)

The secondary lithium battery market is where the biggest growth is expected. Secondary batteries allow for longer life and multiple uses. Rechargeables can be used in high current applications where a primary battery would die quickly and need to be replaced. Currently, however, secondary lithium batteries are primarily in the developmental stage. A few applications have been found and the number is likely to grow. There are two different types of lithium secondary batteries: lithium-ion and lithium polymer. The lithium ion battery employs a novel idea. Neither the cathode or the anode is lithium. The lithium is contained ionically in the solvent. When the battery is charged, the ions deposit themselves as metallic lithium in the electrode. During the discharge, the lithium inculcated in the electrode reverts to the ionic form, creating an electric current. (15) The lithium polymer battery also uses an innovative design. This battery employs a solid electrolyte, a polymer of some sorts. With the lack of a liquid electrolyte, this battery has several advantages, such as not leaking a potentially toxic electrolyte and flexible geometry, which makes thin film batteries possible. (13) Lithium batteries have uses in the notebook computer industry. Being light and powerful, lithium batteries are ideal for use in notebook computers, where weight and space are important considerations. It is projected that many new Pentium™ notebooks will be equipped with lithium-ion batteries, and that lithium batteries will start to dominate notebooks. (17) Another use is in cellular phones. Lithium battery's lightweight and low self-discharge rate make lithium an ideal choice for cellular phones. (18)

The aspects of lithium recycling are not fully known. Yet, given its cost and expected increase in use, lithium battery recycling has potential in the future.

6.0 Future Use of Lithium

The future use of lithium is tied strongly to the health of the chemical, aluminum, and glass industries. As long as these industries perform well, demand for lithium will be present. Yet, the battery industry appears to be the new emerging use of lithium that could potentially become a large market for the metal.

Much new research has gone into the field of lithium batteries. Lithium batteries could be used in car batteries, thin film batteries for computers, and a host of other applications. At Oak Ridge

National Laboratory (ORNL), research is being conducted to develop a thin film lithium battery, which can be placed on almost any substrate. Cars and computers which are coated with thin film lithium batteries are possibilities that come to mind here. Other microelectronics could be possible with this technology. (14) Other research includes the work at Lawrence Berkley National Laboratories (LBL) to advance electric vehicle technology. LBL is looking into lithium-polymer batteries as a power source for electric vehicles, because they have developed several new solid electrolytes and cathodes for lithium batteries. Eventually, they hope to produce an economically feasible battery for electric cars. Hurdles to feasible electric cars are limited range, weight, and space. Researchers at LBL think lithium batteries can overcome these hurdles. However, in the future they hope to replace the lithium with sodium, a metal that is chemically similar to lithium but much more plentiful. (16) Other research into lithium polymer batteries is being performed by several groups, some with the United States Advanced Battery Consortium, a group of private industry and governmental associations. The first of these groups consists of Argonne National Labs, Hydro-Quebec, and 3M. This group works with the USABC. Another group working with the USABC is W.R. Grace and Johnson Controls. A third group, A.C. Delco and Valence Technologies, are working independently to develop lithium polymer batteries. (13)

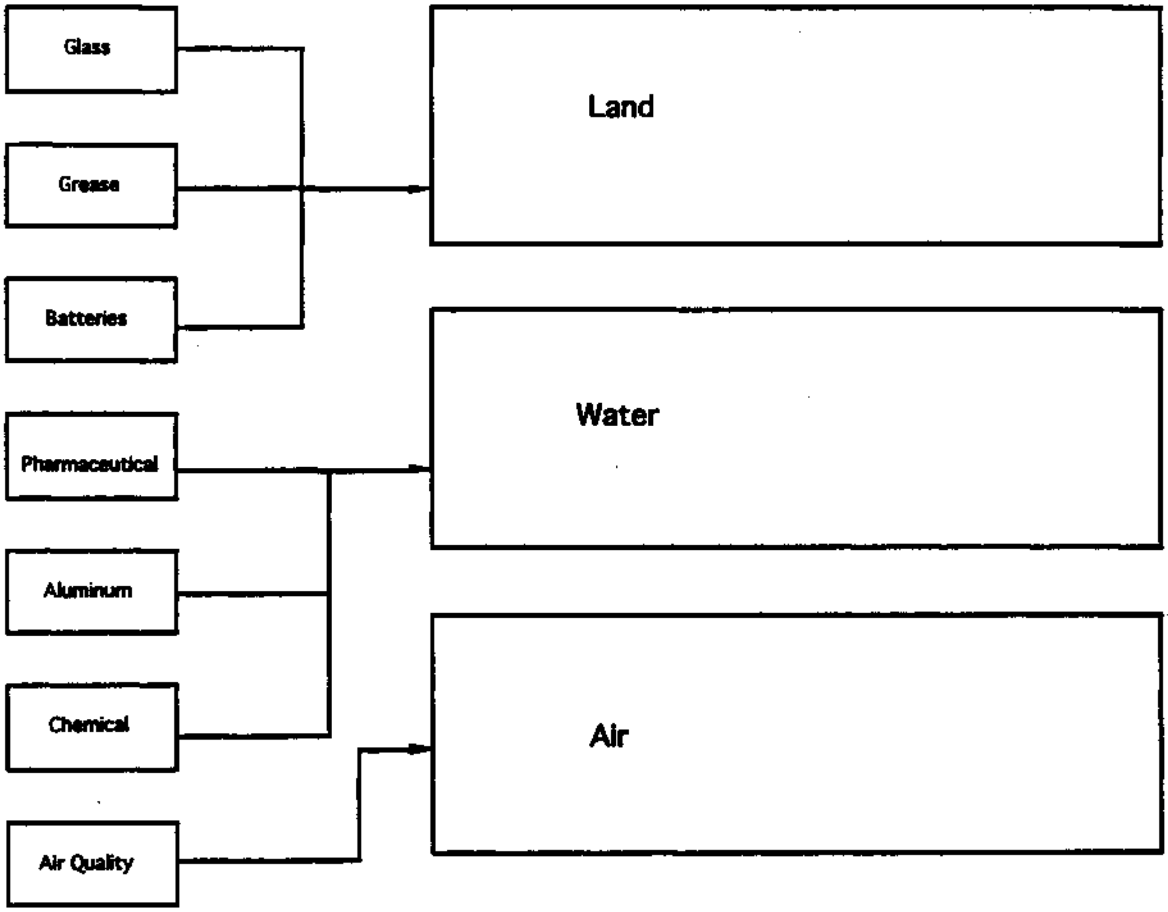
7.0 Lithium Sinks

With the lack of any evidence to the contrary, almost all of the lithium that is produced in the United States is dissipated into the environment. There is no accounting of the lithium by the appropriate industries, and judging by the processes employed, the likelihood of lithium recycling is minimal.

7.1 Lithium in the Environment

Lithium in the environment from the aluminum industry goes primarily to the water, because of the manner in which the spent cells are recycled. The chemistry of the situation leads to the conclusion that the lithium is thrown into the wastewater stream. It is likely that the chemical industry also leaks lithium into the water, since lithium chloride is produced which is likely discharged with the wastewater stream. The air quality industry has leaks to the air during operation and likely to water after disposal of spent units. The battery industry and glass industry likely have most of their disposal to the land, as batteries and glass are disposed into landfills after use. Pharmaceuticals discharge to the water much like chemical plants and directly into humans through the drugs administered, both intentionally and unintentionally, through fugitive emissions. The lithium in grease is likely a land pollutant, because greased items are often thrown away into landfills after usage.

Possible Environmental Sinks for Lithium



8.0 Recommendations

Further study is warranted into the use of lithium as a material. In my opinion, most of that study should be directed toward the health effects of lithium. Lithium could be an environmental disaster waiting to happen, but only if the health effects are severe at relatively low dosages. However, lithium exposure for most people is small. After a proper determination of the possible health effects is completed, further research can be invested into precise accounting of the lithium. If the health effects are found to be severe, study should be directed toward fugitive emissions in each of the various industries. Then, thought could be directed toward policy decisions and proper design considerations.

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