Battery Recycling: defining the market and identifying the technology required to keep high value materials in the economy and out of the waste dump

By

Timothy W. Ellis
Abbas H. Mirza

Introduction:

The accumulation of post consumer non-Lead/Acid batteries and electrochemical (n-PbA) cells has been identified as a risk in the waste stream of modern society. The n-PbA's contain material that is environmentally unsound for disposal; however, do represent significant values of materials, e.g. metals, metal oxides, and carbon based material, polymers, organic electrolytes, etc. The desire is to develop systems whereby the nPbA's are reprocessed in a hygienic and environmentally astute manner which returns the materials within the n-PbA's to society in an economically and environmentally safe and efficient manner. According to information published in the Fact File on the "Recycling of Batteries" by the Institution of Engineering and Technology (www.theiet.org) the following, Table 1, describes the recycling market.

Table 1: Recoverable Metals from Various Battery Types

Battery Type	**Recycling**
Alkaline & Zinc Carbon	Recycled in the metals industry to recover steel, zinc, ferromanganese
Nickel – (Cadmium, Metal Hydride)	Recycled to recover Cadmium and Nickel with a positive market value
Li-Ion	Recycled to recover Cobalt with a positive market value
Lead-Acid	Recycled in Lead industry with a positive market value
Button Cells	Silver is recovered and has a positive market value; Mercury is recovered by vacuum thermal processes

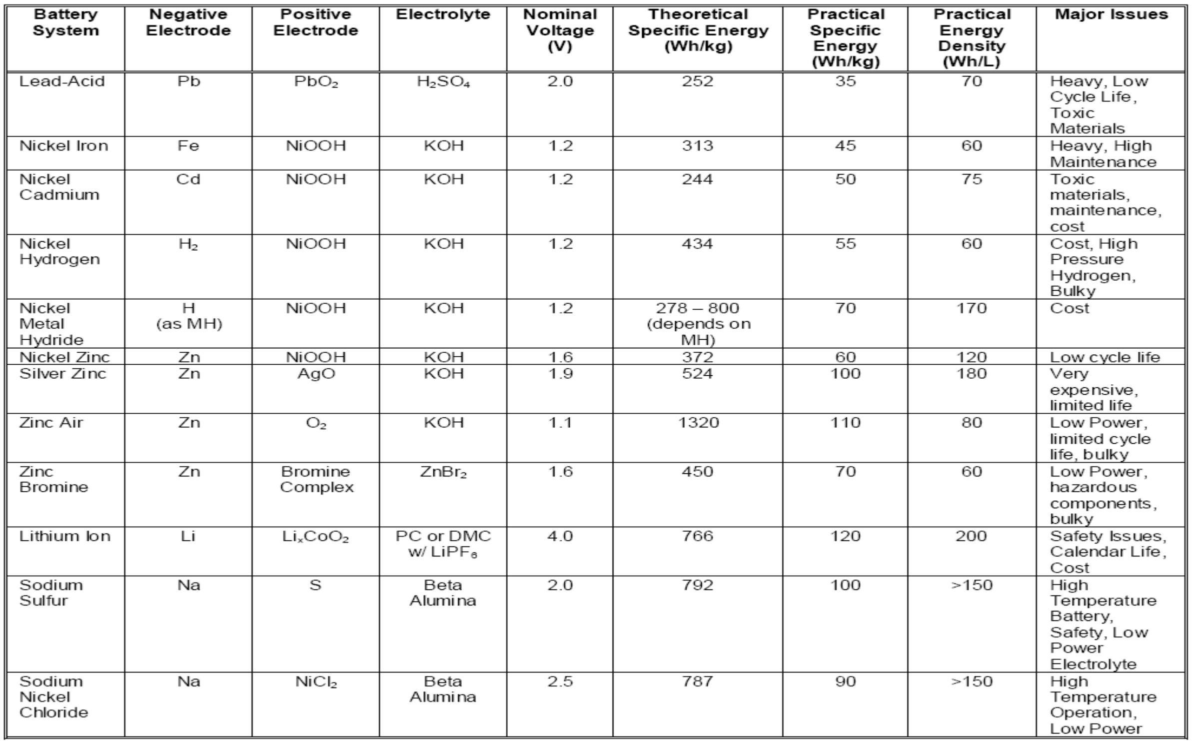
A literature search on "Recycling and Battery" on the STN Easy data base produced over 2500 hits. During the same search process the World Patent Index (WPINDEX) indicated 317 patents recorded in the art.

Materials used in n-PbA Application

Although many types of n-PbA cells are sold commercially the basic material set is really rather limited, although a greater number of small alloy additions or tramp elements maybe present, Tables 2 & 3. Appendix 1 has a listing and schematics of common n-PbA cells.

The basic n-PbA material stream is dominated by Zn, Mn, Ni, Cd and Fe containing chemical species. Plastics, polymers and paper are also contained but can be removed by various classification techniques, e.g. density, electrostatics. Other high value materials are also present within the stream, e.g. Co, Ag, in addition to element considered harmful to the environment e.g. As, Hg, F, Cl. It would be desirable to develop a processing flow sheet which allows for separation of the various constituents into high quality products which would be directly saleable in the present market structure.

Table 2: Tradeoff Table of Various Primary and Rechargeable Technologies



Battery System	Negative Electrode	Positive Electrode	Electrolyte	Nominal Voltage (V)	Theoretical Specific Energy (Wh/kg)	Practical Specific Energy (Wh/kg)	Practical Energy Density (Wh/L)	Major Issues
Lead-Acid	Pb	PbO_2	H_2SO_4	2.0	252	35	70	Heavy, Low Cycle Life, Toxic Materials
Nickel Iron	Fe	NiOOH	KOH	1.2	313	45	60	Heavy, High Maintenance
Nickel Cadmium	Cd	NiOOH	KOH	1.2	244	50	75	Toxic materials, maintenance, cost
Nickel Hydrogen	H_2	NiOOH	KOH	1.2	434	55	60	Cost, High Pressure Hydrogen, Bulky
Nickel Metal Hydride	H (as MH)	NiOOH	KOH	1.2	278 – 800 (depends on MH)	70	170	Cost
Nickel Zinc	Zn	NiOOH	KOH	1.6	372	60	120	Low cycle life
Silver Zinc	Zn	AgO	KOH	1.9	524	100	180	Very expensive, limited life
Zinc Air	Zn	O_2	KOH	1.1	1320	110	80	Low Power, limited cycle life, bulky
Zinc Bromine	Zn	Bromine Complex	$ZnBr_2$	1.6	450	70	60	Low Power, hazardous components, bulky
Lithium Ion	Li	Li_xCoO_2	PC or DMC w/ $LiPF_6$	4.0	766	120	200	Safety Issues, Calendar Life, Cost
Sodium Sulfur	Na	S	Beta Alumina	2.0	792	100	>150	High Temperature Battery, Safety, Low Power Electrolyte
Sodium Nickel Chloride	Na	$NiCl_2$	Beta Alumina	2.5	787	90	>150	High Temperature Operation, Low Power

Table 3: Metals Inventory from Recycling Common Primary & Rechargeable Batteries

Base Element	**Cell Type**	**Species**
Zinc	Zinc-Carbon	Zn, $ZnCl_2$, $Zn(OH)_2$
	Alkaline-Manganese	Zn, ZnO
	Nickel Primary	Zn, ZnO
	Zinc-Air	Zn, ZnO
	Silver-Zinc	Zn, ZnO
Manganese	Zinc-Carbon	MnO_2, MnOOH
	Alkaline-Manganese	MnO_2, $Mn(OH)_2$
	Nickel Primary	MnO_2, MnOOH
	Lithium Primary	MnO_2
Nickel	Nickel Primary	NiOOH, $Ni(OH)_2$
	Nickel-Cadmium	NiOOH, $Ni(OH)_2$
	Nickel-Metal Hydride	NiOOH, $Ni(OH)_2$, $LaNi_5$
Cadmium	Nickel-Cadmium	Cd, $Cd(OH)_2$
Silver	Silver Oxide	Ag, Ag_2O
Lithium	Lithium Primary	Li, $LiMnO_2$
	Lithium Ion	$LiCoO_2$, LiC
Cobalt	Lithium Ion	$LiCoO_2$
	Nickel-Metal Hydride	$La(Ni, Co)_5$
Carbon	Zinc-Carbon	C
	Lithium Ion	C, LiC
Other Element		
Copper	All	Electrodes
Iron	All	Casings
Plastics	All	Packaging
Mercury	Zn, Cd containing	Addition, Contaminant
Aluminum	All	Packaging, Electrode
Tin	Zinc, Manganese, Nickel	Electrodes
Organic Electrolyte	Li Based	Electrolyte
Tetra-Fluoro Salts	Li-Based	Electrolyte

Table 3a: Composition Matrix for Cell Types by Weight %

	Metal									**Electrolyte**					**Other**
System	**Pb**	**Ni**	**Cd**	**Zn**	**Mn/Co**	**Ag**	**Hg**	**Li**	**Fe**	**H_2SO_4**	**KOH**	**NH_4CL**	**Organic**	**H_2O**	**Packaging**
Pb/PbO_2	65									8				17	10
Ni-Cd		20	15						45		5			10	5
Zn/MnO_2				20	25				20		-	5		10	20
Alkali				20	30				20		5	-		10	15
Zn/Ag_2O				10		30	1		40		3			6	10
Zn/HgO				10			2		45		3			6	11
Zn/O_2				30			2		45		4			8	12
$Li/Li(Co, Mn)O_2$					30			2	50				10		10

A comparison of the battery market as a percentage of the total consumption of several metals is now made against Pb. This may possibly be important data to determine whether recycling would have a major or minor impact on market dynamics if recycling was to take hold.

Table 4: Batteries Usage as a % of Metal market Consumption:

Metal	**% Of Metal Market Consumption**
Cobalt	20
Zinc	<10
Nickel	4
Lithium	20 (2005), 9 (2000)
Manganese	<2
Cadmium	80
Lead	70

Inspection of Table 4 indicates that battery usage and presumably recycling from battery usage has a strong effect on market prices for Cd and as it does for Pb. The emerging consumption of both Li and Co in Li-ion technology and therefore recycling from the usage of Li technology may have ever high effects and affects on the market for these metals. The market pricing of Zn, Mn and Ni would appear to be largely independent of reclamation from battery recycling.

Market Data for n-PbA:

Finding the tonnage? The question remains as to the total market available for recycling n-PbA cells. Unfortunately, most market data is reported as the total number of cells or the economic value of the primary purchase of those cells, not the mass of material involved. In discussion with Tim Warren of the RBRC in the U.S. approximately 5M lbs of cells passed through their collect scheme in 2005. GRS Batterien the German recycling organization has published in its 2005 success monitoring document some data useful in understanding the dynamics of the recycling enterprise. Although each country will have its own specifics, these results may serve as a point of planning.

Table 5: Circulation vs. Collection vs. Recycling for 2005 by Individual Battery Type

	Volumes in Kg			**Reclamation Metrics.**		
Type	**Circulation**	**Collected**	**Recycled**	**Collected/Total**	**Recycle/Total**	**Recycled/Collected**
PR ZnC	4554842	2937621	2683210	0.645	0.589	0.913
PR Alk	22140128	5851837	4732160	0.264	0.214	0.809
PR ZnAir	5053	0	0	0.000	0.000	0.000
PR Li	216526	202216	167529	0.934	0.774	0.828
Total	26916549	8991674	7582899	0.334	0.282	0.843
PBAgO	40068	5731	5361	0.143	0.134	0.935
PBAlMn	163300	23358	21849	0.143	0.134	0.935
PBZnAir	59553	8518	7968	0.143	0.134	0.935
PBLi	169080	24185	22622	0.143	0.134	0.935
Total	432001	61793	57800	0.143	0.134	0.935
PBlZnAir	48410	196207	107760	4.053	2.226	0.549
PBlZnC	162604	828560	348160	5.096	2.141	0.420
PBlAlMn	22256	51907	56371	2.332	2.533	1.086
PBlLi	2453	0	0	0.000	0.000	0.000
Total	235723	1076674	512291	4.568	2.173	0.476
SR-Li	2212348	65770	0	0.030	0.000	0.000
SRNiMH	1921010	78470	69860	0.041	0.036	0.890
SRNiCd	1830150	908132	783920	0.496	0.428	0.863
SRAlMn	40642	0	0	0.000	0.000	0.000
Total	6004150	1052372	853780	0.175	0.142	0.811
SBNiCd	295	0	0	0.000	0.000	0.000
SBNiMH	12789	0	0	0.000	0.000	0.000
Total	13084	0	0	0.000	0.000	0.000
SPbA	1015389	1080431	903860	1.064	0.890	0.837
Total	**68218403**	**23445457**	**18917400**	**0.344**	**0.277**	**0.807**

PR = Primary Cell Round
PB = Primary Cell Button
PBL = Primary Block Cell < 500g
SR = Secondary Cell Round
SB + Secondary Cell Button
SPbA = Small Pb-Acid Cell

Table 6: Circulation vs. Collection vs. Recycling for 2005 by Individual Battery Type

Type	Total Circulation	Total Collected	Total Recycled	Collected/Total	Recycle/Total	Recycled/Collected
ZnC	4717446	3766181	3031370	0.798	0.643	0.805
AlK	22366326	5927102	4810380	0.265	0.215	0.812
ZnAir	113016	204725	115728	1.811	1.024	0.565
Li	2600407	292171	190151	0.112	0.073	0.651
NiMH	1933799	78470	69860	0.041	0.036	0.890
NiCd	1830445	908132	783920	0.496	0.428	0.863
PbA	1015389	1080431	903860	1.064	0.890	0.837
Total	**34576828**	**12257213**	**9905269**	**0.354**	**0.286**	**0.808**

Table 7: Available Tonnage for Recycling Germany 2005

Type	Circulation/Total	Collect/Total	Recycled	Kg for Recycle	Metric Tons
ZnC	0.136	0.307	0.247	2449703	2449.7
AlK	0.647	0.484	0.392	3887353	3887.4
ZnAir	0.003	0.017	0.009	93522	93.5
Li	0.075	0.024	0.016	153665	153.7
NiMH	0.056	0.006	0.006	56455	56.5
NiCd	0.053	0.074	0.064	633500	633.5
PbA	0.029	0.088	0.074	730425	730.4
			Total	8004622	8004.6

Upon inspection of the data presented by GRS, collection rates for primary batteries are much higher than that for secondary types. Ni-Cd based cells have higher rates of recycling than all other. This is not surprising given the long standing concern with Cd entering the environment. Table 8 compares recycling rates on a chemistry basis. Given the present pricing of Zn ($7000/ton) and Ni ($30000/ton), the value of the Zn and Ni recovered is about equal. Market growth is still possible in all areas as total recycling rates are still below 30%.

Table 8: Recycling rate based upon Cell Chemistry.

Type	Total Circulation	Total Collected	Total Recycled	Collected/Total	Recycle/Total	Recycled/Collected
Zn Base	27196788	9898009	7957478	0.364	0.293	0.804
Li Base	2600407	292171	190151	0.112	0.073	0.651
Ni Base	3764244	986602	853780	0.262	0.227	0.865
PbA	1015389	1080431	903860	1.064	0.890	0.837

Although this data is for Germany, it may serve as a good benchmark for the G7 nations. The Personal Purchasing Power (PPP) of a German citizen is $30500 U.S. according to data by the IMF. Given that Germany has a population of approximately 82.5M, each German is buying in the range of 0.41Kg of batteries. However, only 0.12 Kg of battery material is being return to the economy.

Market Opportunity

The size of the market opportunity is a combination of metals prices and mass of material in the consumer market. Since battery grade material has higher pricing point than commodity this should serve as the upper bound of the pricing available for recycled materials. For reference the mass of material available in total for this calculation is based upon Germany 2005 data. Pricing data was gathered by phone interview with established vendors servicing the battery industry.

Table 9: Market Opportunity Data, based on Germany 2005

Metals	Content	Tonnes for recycle	$/Kg	Market $M	Pricing Source
Zn	0.2	5439.36	3.50	$19.04	LME
MnO2	0.3	8159.04	1.80	$14.69	Tronox
LiCoO2	0.3	780.12	30.00	$23.40	OM
Ni	0.4	1505.70	40.00	$60.23	Inco/CVRD
		15884.21	Total	$117.36	
			Average $/Kg	$7.39	

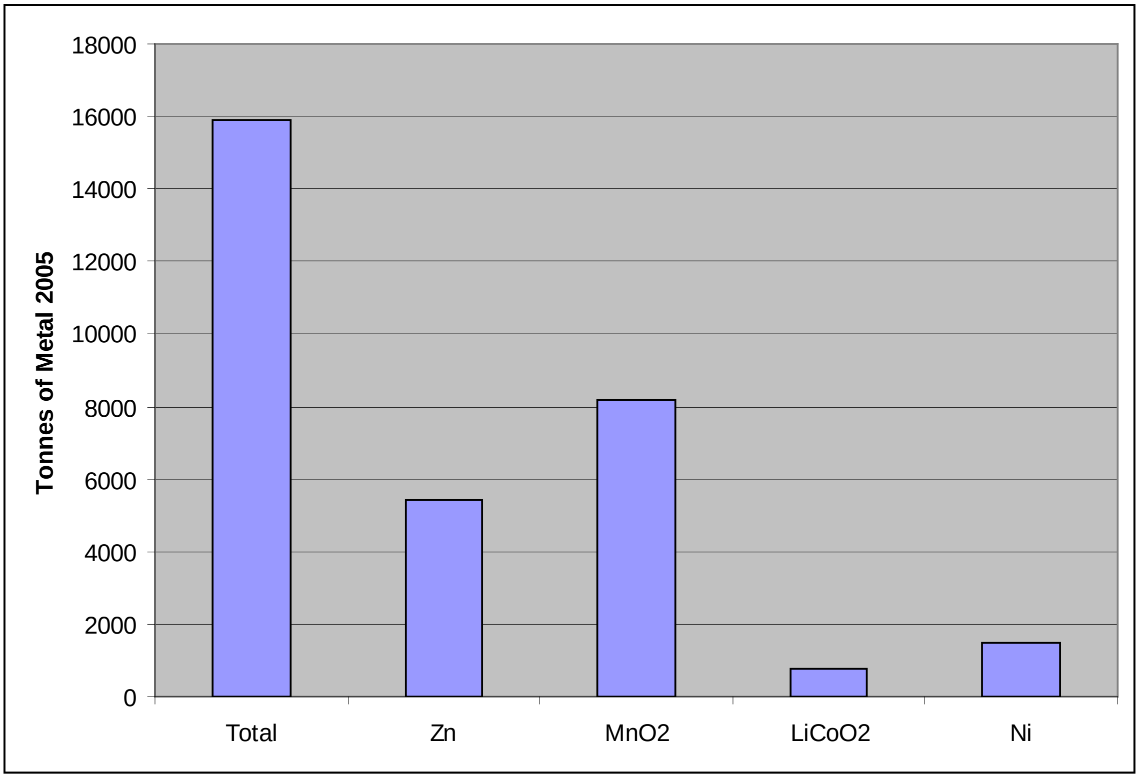


Figure 1: Mass of Metallic's for Recycling

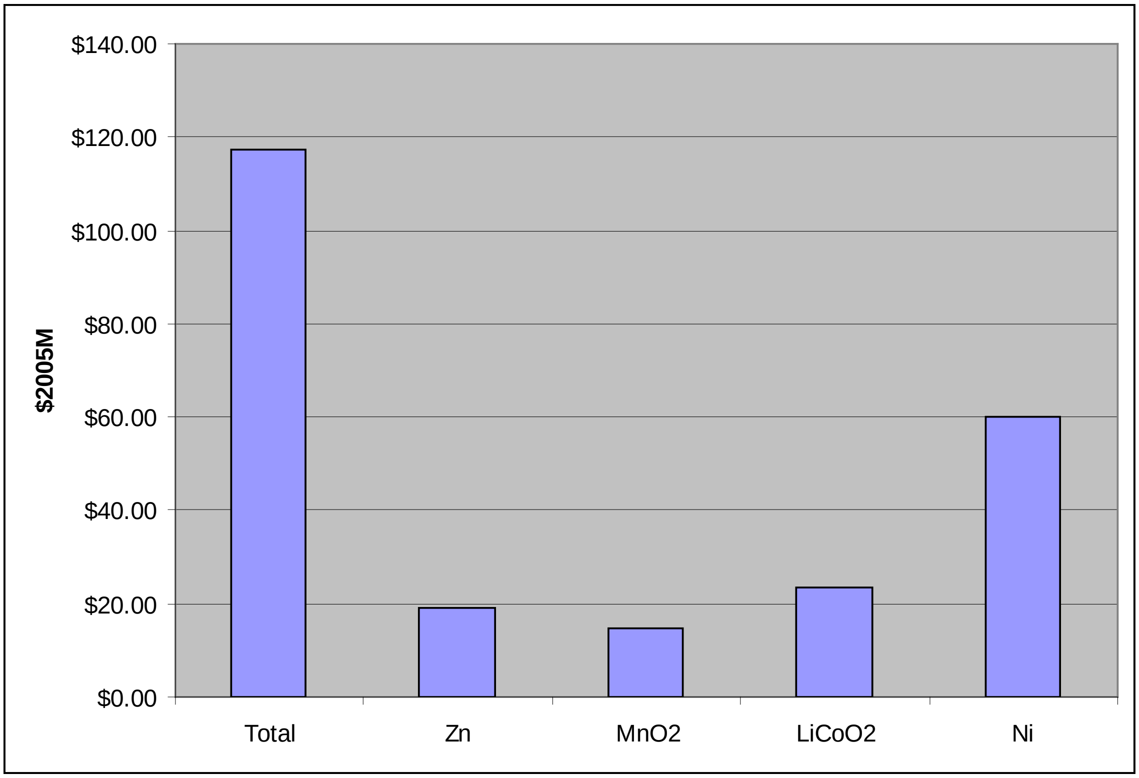


Figure 2: Economic Value of Metals 2005, Computed as Battery Grade Material

Zn and MnO_2 predominate the mass volume amounts in the recycled battery stream. While the highest $ U.S. value materials are the refractory metals, i.e. Ni and Co. In total $ U.S. value Ni based batteries represent the largest opportunity followed by Zn and Li ion. Given the fact the value of $LiCoO_2$ is an order of magnitude higher than the combined Zn/MnO_2 per mass unit the Li based material represents a higher value added stream for recovery by recycling methods.

Companies Involved in Recycling Rechargeable Batteries:

A number of companies around the world are licensed and are receiving n-PbA batteries for recycling. Most facilities use conventional pyrometallurgical processing techniques to produce metals for re-alloying during the production of commercial metals.

Table 10: Facilities Engaged in n-PbA Recycling

Company	**Battery Types**	**Process**	**Location**
Umicore	All + E-Scrap	Pyrometallurgy + Electrowin	Hooboken Bel
Toxco	Li, Ni Based	Cyromilling (Li), Pyrometallurgy (Ni)	Trail BC Baltimore OH
Dowa	All + E-Scrap	Pyrometallurgy	Japan
CVRD (INMETCO)	Ni Based	Pyrometallurgy	Ellwood City Pa
RMC	All	??	ON
Salesco Sytems	All + Hg	Pyrometallurgy	Phoenix, AZ
Bethlehem Apparatus	Hg Based	Pryrometallurgy	Hellertown PA
XStrata	All + E-Scrap	Pryrometallurgy, Electrowin	Horne Que, Nikkelverk Nor, Sudbury Ont
Toho Zinc	Ni-Cd, Ni-MH	Pyrometallurgy	Onahama Jp
Japan Recycle Center	All	Pyrometallurgy	Osaka Jp
OnTo Technology	Li	Solvent Extraction (CO_2)	Bend OR
Accurec	All	Pyrometallurgy (V)	Mulhiem GDR
Korea Zinc	Ni-Cd	Electrowin	Onsam, Kor
SNAM	Ni-Cd, Ni-MH, Li	Pyrometallurgy (V)	Saint Quentin Fallavier Fr
AERC	All + Hg	Pyrometallurgy	Allentown PA, Hayward CA, West Melbourne FL.
NIREC	Ni Based	Pyrometallurgy	Dietzenback
Erachem (Revatech)	Mn	Pyrometallugy	Terte Bel.
DK	All	Pyrometallurgy	Duisburg GR
GMA &CO	Zn Based	Pyrometallurgy	
NQR	Hg	Pyrometallurgy (V)	Lubeck
REDUX	Zn based	Pyrometallurgy	Dietzenbach
Varta	??	??	Hanover GR
Batrec AG	Li, Hg	Pyrometallurgy	Wimmis, CH
SAFT-NIFE	Ni Based	Pyrometallurgy	Oskarhamn, SW
AEA Technology	Li	?	Sutherland Scotland
IPGNA Ent. (Recupyl)	All	Hydrometallurgy	Grenoble, FR
AFE Group (Valdi)	All	Pyrometallurgy	Feurs, FR, La Palais sur Veine, FR
Citron	All	Pyrometallurgy	Zurich CH, Rogerville, FR
Zimaval (Cite Plus, Suez SA)	Zn, Mn, Hg	Hydrometallurgy	Falaise FR
Euro Dieuze/SARP	All	Hydrometallurgy	Lorraine FR
Seche Environmental (Tredi)	Cd, Hg	Pryometallurgy	Salaise sur Sanne
EBS	Zn Based	Hydrometallurgy	Austria

Recycling at this time is heavily biased toward Ni-Cd chemistries and an extension into Ni-MH. Li based system is receiving some attention. At this time Zn, i.e. Zn-C, alkaline based systems batteries are sent directly to land fills.

System for the Discharge of Residual Power:

As batteries are electrochemical cells, the amount of electrochemical potential remaining in the cell prior to recycling may be an issue. Cells with residual electrochemical power imply that the materials within the cell are still reactive and operations as such breaking the cells may allow for the uncontrolled release of chemical energy. Li metal within a Li-ion cell is very reactive toward air or the electrolyte within the cell or with H_2O, acid and bases used as electrolytes in other battery types if they are sent through the breaker at the same time. Several systems have been proposed to reduce the hazard of cells which are not fully discharged.

The first system is to break the cells under an inert environment such as CO_2 or N_2 thereby preventing air from initiating a reaction. This however does not reduce uncontrolled reactions with materials within the recycle stream. Cryomilling, i.e. cooling the batteries prior to breaking to a very low temperature, is used by Toxco for the recycling of Li-ion cells. They first cool the cells to -325F (-175C) which is liquid N_2 temperatures prior to breaking as this reduces the rate of any chemical reactions. Additionally the N_2 serves as an inert environment. In the Toxco process, alkali is added in a controlled manner to react with the Li metal.

Other workers in the area have used agitated H_2O baths which contain Iron particles, although other conductive media may be applicable. The agitation cause intermittent dead shorting of the cells which allows for their discharge while the water serves as a thermal sink for the heat generated during discharge. As similar system could be envisioned using weak or high dilutions of strong electrolytes in H_2O solution such as Citric Acid, Acetic Acid, Acetates or Hydroxides. As a point of concern, some consideration needs to be shown to picking electrolytes which will not complicate further processing, e.g. halogen salts, NaCl which would add Cl to the waste stream.

Type Sorting of Batteries:

To maximize the efficiency of n-PbA recycling, sorting of the batteries according to chemistry would helpful. All consumer batteries are bar coded, and since 1997, Zn-based consumer cells have a UV designation marking. The question remains as to what physical principles can be used to determine the difference between the materials contained within the cells. It would be desirable for this analysis to be non-destructive, i.e. possible on the cells prior to breaking to facilitate safe handling and storage prior to processing. Among the possibilities are X-ray radiography, X-ray fluorescence, eddy current, ultrasonic attenuation, reading the bar codes on the cells, cell density and size, Label reading, etc. Essentially a system to perform the separation and recombining of like chemistries would follow Figure 3.

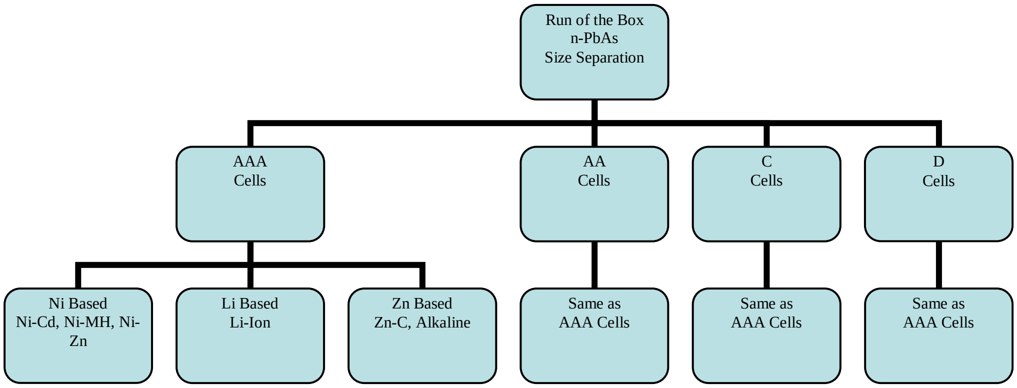


Figure3: Separation by Size and Chemistry

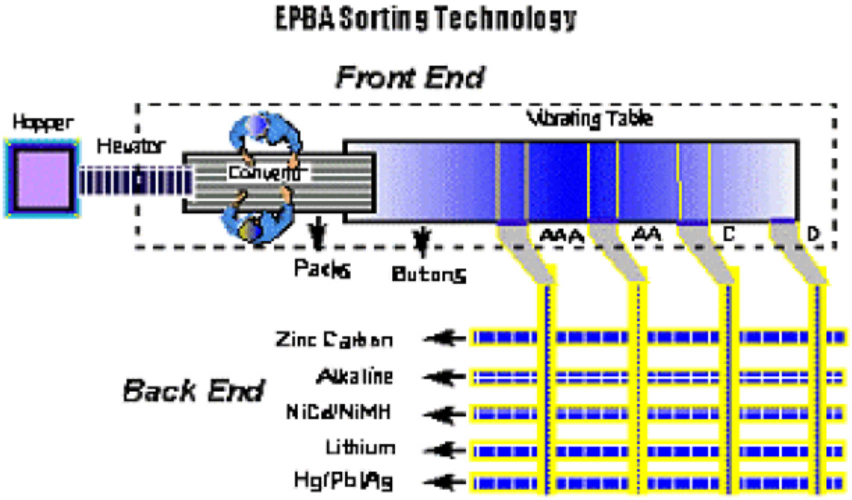


Figure 3a: Sorting Schematic form GRS Batterien,

Several companies have produced sorting systems to recycle batteries, e.g. Euro Bat Tri, Mitsubishi. The following system, developed by Mitsubishi, can serve as a model for one designed specifically for the task at hand. It is unknown at this time if this is a “one off” or commercially available. A similar system could be constructed using off the shelf components available in the U.S. and Europe.

The outline presented here follows the Mitsubishi Battery Sorter apparently installed in Japan. This is a system to sort the batteries according to the types so that the batteries containing precious resources may be recycled efficiently. The electromagnetic sensor, specific to Mitsubishi, identifies the internal structure and component substances of used batteries, and sorts them at high speeds.

Principle of the Electromagnetic Sensor: When the excitation coil applies a high-frequency magnetic field to the battery, eddy current is generated in the battery. Since the eddy current generated in the battery differs for each internal structure and component substance of the battery, changes in the magnetic field caused by the eddy current are detected by a detector coil which makes it possible to identify the battery type.

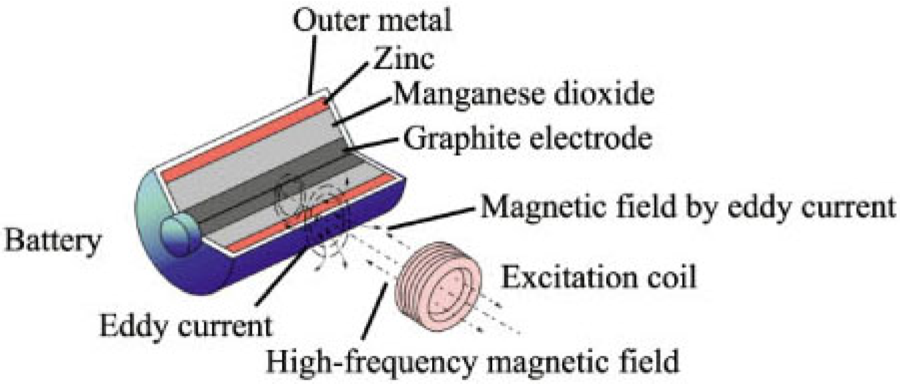


Figure 4: Principle of electromagnetic induction method

This system consists of the storage hopper, feeding conveyor, aligning machine, transfer conveyor, electromagnetic sensor and battery discharge mechanism (air jet). The batteries are aligned and supplied into the electromagnetic sensor one after another at high speeds by a rotary sorter. The electromagnetic sensor specific to Mitsubishi is capable of identifying the internal structure of the battery in a non-destructive and non-contact way. The batteries identified are discharged by air jet securely.

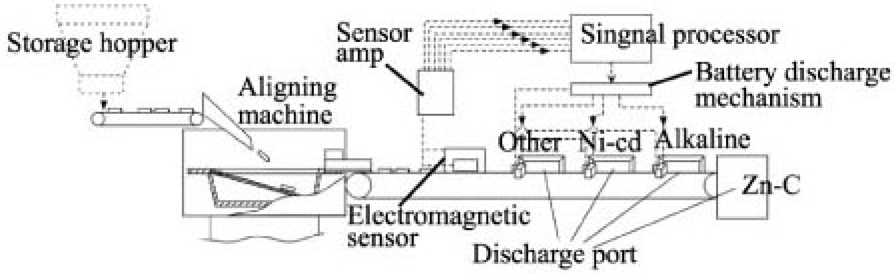


Figure 5: Battery Sorter Schematic

Table 11: Performance of Mitsubishi Battery Sorter

Metric of Performance	**Performance**
Cell Size	AA, C, D
Chemistry	Zn-C, Alkali, Ni-Cd
Sorting Performance	>95%
Capacity	D > 2.5 tons/hr, AA > 0.35 Tons/Hr: > 5 Cells/Sec

This system is delivered to a smelting manufacturer in Gumma Prefecture, and is used to sort the batteries recovered from around the city in an accurate way. Sorting of batteries, which used to be done manually, has been automated by introducing this system. Therefore, it is possible now to treat a huge amount of batteries at a time.

Metallurgical Processing Technology for n-PbA

In this section, we will delve into the processing techniques used in the industry for reprocessing n-PbA. This is not only to serve as a technology introduction but also to compare techniques on an equal footing for the design of process flows.

Pyrometallurgical Techniques:

Pyrometallurgical reclamation of Ni Based Materials:

The INMETCO facility in Ellwood, PA, will be used as a model for recycling of Ni based materials from batteries. Ni will be present in two forms as the mixed oxide NiO/NiOOH and/or as metal and alloy, e.g. Ni foam/screen/sheet, $LaNi_5$ alloy. To produce metal, the NiO/NiOOH must be reduced to Ni. This can be accomplished by carbothermic reduction. The $LaNi_5$ type alloys with the alloying element, e.g. La, Sn, Mn, Co, may be reduced to metal and dissolved in the Ni melt, e.g. Sn, Co, etc. or floated off in the slag/fumes, e.g. La, Mn. The subsequent metal can be further purified by electro refining or the Mond process discussed elsewhere in this document. However, battery manufacturers prefer primary Ni for cell construction. Therefore, most of the Ni produced is used directly in the production of stainless steel. The perception is that other battery streams treat the Ni containing materials in the same fashion, e.g. Umicore, Korea Zinc, Dowa, Toxco, INMETCO. Although, Ni-Cd cells are processed in the same stream, several facilities have dedicated Cd recovery systems to reclaim Cd from the fumes and off gasses, e.g. INMETCO, Korea Zinc, Umicore.

Pyrometallurgical Vaporization for the Removal of Cadmium (Cd), Mercury (Hg) and/or Zinc (Zn):

Metals with high vapor pressures can be removed by conventional pyrometallurgical processing or vacuum distillation operations. At elevated temperature Cd, Hg and Zn can be removed by vaporization with or without the utilization of vacuum as shown in Figure 4. This unit operation is done in the primary smelting of Cd, Hg and Zn ores. ZnO is carbothermically reduced above 935C. at 1 atm. By reducing the pressure to 0.5 atm, the reaction is favorable at 900C. This is higher than the boiling point of Zn which is now reduced to 840C. Therefore, recovery of Zn from ZnO in post consumer batteries should follow primary metallurgical practice. The vapor pressure of Cd, Hg and Zn metal is higher than that of the oxides; therefore it is desirable to reduce the various compounds of these metals to metal. Much of the Cd and Zn in spent n-PbA will be present as oxides as such the application of carbothermic reduction and retorting is an option. At this time, several recyclers are producing Cd from n-PbA waste by vaporization, e.g. SNAM, Accurec, Toho Zinc. In the high temperature process used in facilities recycling Ni based n-PbA's, the volatile Cd and Zn are fumed off and presumably captured in the flue dust of the operations for reprocessing following normal procedures. Hg based cells are usually sent to certified Hg recycling operations and are handled as a toxic material. The Hg operators seem to be smaller and independent of the large firms doing primary and secondary metals winning. After removal of the Cd from Ni-Cd cells, the remaining metals are sent to convention secondary Ni smelters to recover the Ni values without the difficulty of handling the Cd. One example of a Hg recycling system for batteries is given by the EPBA a schematic of which follows in Figure 5.

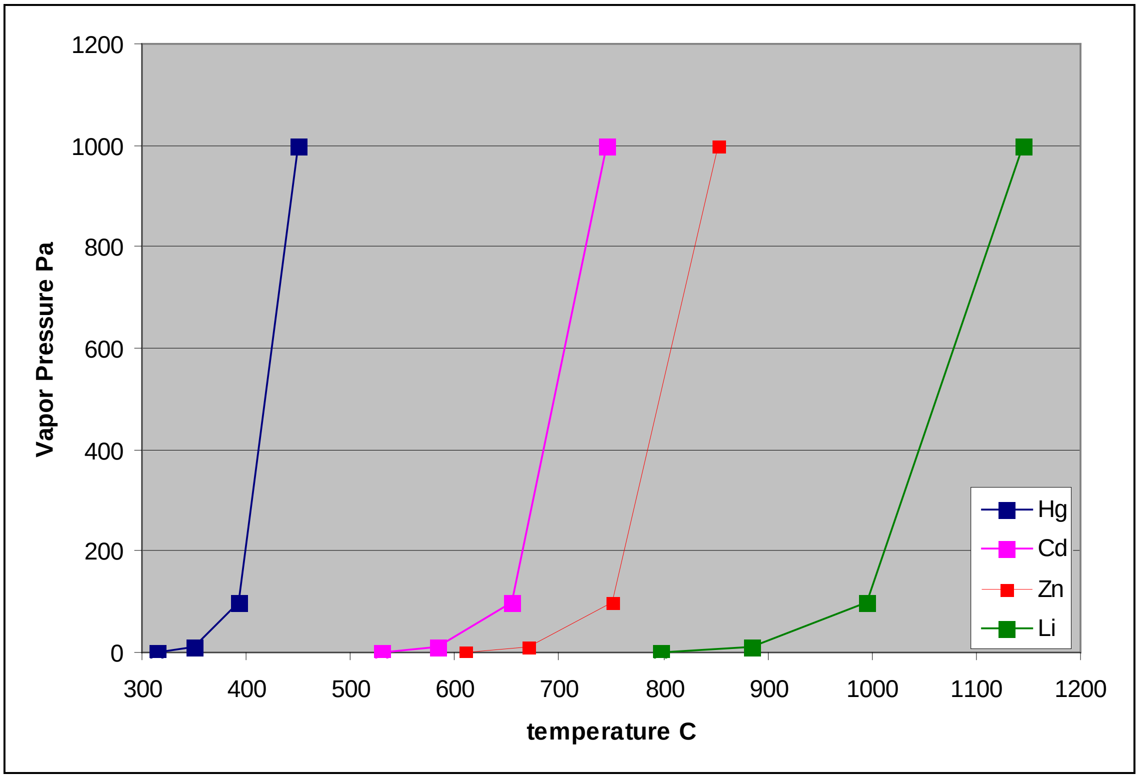


Figure 6: Vapor Pressure Curves for Cd, Hg, Zn and Li.

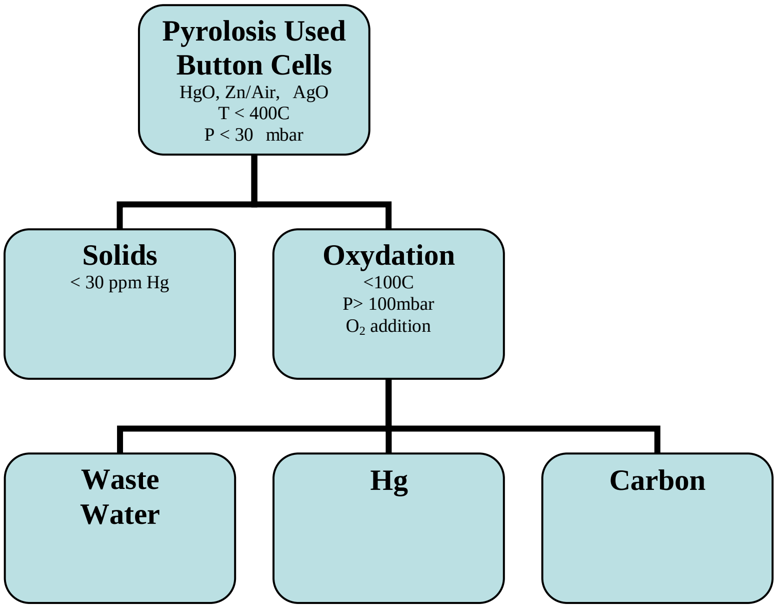


Figure 7: Hg Battery Processing Scheme

Solvent Extraction Techniques:

Removal of Electrolytes from Lithium Based n-PbA's:

Several electrolyte systems are presently used in n-PbA's based upon Lithium (Li) chemistry. Lithium, an alkali metal, is very reactive when exposed to H_20, organic and/or inorganic acid and bases thereby presenting a hazard to recycling operations. The electrolytes in present Li batteries are in three general chemical families; 1) organic carbonates, e.g. Propylene, ethylene, Diethyl, Dimethyl, 2) Dimethyl oxyethane, or 3) Li Tetrafluoro salts, e.g. Arsenate, Phosphate, and Borate (1). OnTo Technology, Bend OR uses Liquid CO_2 (3) to remove the electrolyte while Toxco in Trail BC neutralizes the Li cells with a cyromilling technique with NaOH neutralization of the Li adducts.

Liquid and/or Supercritical Carbon Dioxide (CO_2) Solvent Extraction:

Leaching of spent n-PbA's by CO_2 for removal of the electrolyte is taught in a patent by Sloop (2, 3). Since liquid and supercritical CO_2 are excellent solvents for non-polar moieties they would be considered suitable for removing organic electrolytes from spent n-PbA. Additionally CO_2 is a very environmentally sound solvent being non-flammable, non-toxic and is also inexpensive.

Supercritical fluids are those which exist above a critical pressure and temperature for a specific substance. These fluids are unique as they represent a state of matter where liquids and gasses become indistinguishable from each other, see Figure 1.

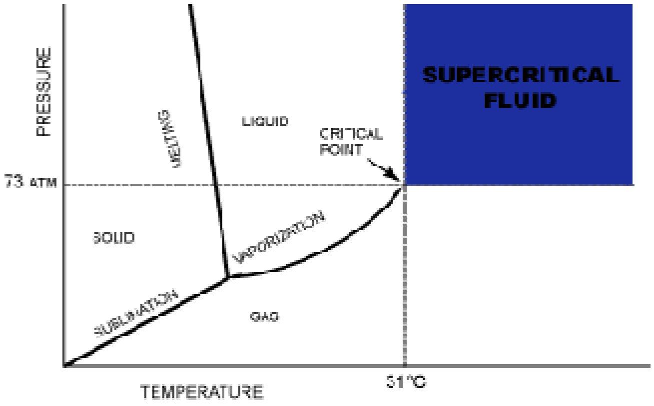


Figure 8: Single Component Phase Equilibria for Carbon Dioxide.

Supercritical fluids have solvation properties of liquids but the low viscosity of a gas making them ideal for the separation of substance by leaching or dissolution operations. Supercritical CO_2 is non-flammable, non-toxic, and inexpensive and has a critical point at relatively low pressures and temperatures; see appendix 1 for a comparison with other systems. It is known to be an ideal solvent for non and low polar materials.

Carboxylation of Transition Metals: The Mond Process:

The Mond Process is a technique which converts nickel oxide (NiO) into pure Ni followed by the reaction of Ni with Carbon Monoxide (CO). This process makes use of the fact that carbon monoxide complexes with nickel readily and reversibly to give Ni tetra-Carbonyl ($Ni(CO)_4$). Ni(CO)4 has a high vapor pressure and can be easily separated from solids by distillation. No other element forms a carbonyl compound under the mild conditions used in the process. Under more aggressive condition carbonyls can be formed of other middle transition metals, e.g. Fe, Co, Cr, Mo, V, W.

This process has three steps:

1. NiO is reacted with Syngas, at 200 °C to remove oxygen, leaving impure nickel. Impurities include iron and cobalt.

$NiO\ (s) + H_2\ (g) \rightarrow Ni\ (s) + H_2O\ (g)$

"Synthesis gas" is produced via the endothermic reaction of steam and carbon:

$H_2O + C \rightarrow H_2 + CO \quad \Delta H = 131\ kJ/mol$

2. The impure nickel is reacted with excess carbon monoxide at 50 - 60 °C to form Ni tetra-Carbonyl.

$Ni\ (s) + 4\ CO\ (g) \rightarrow Ni(CO)_4\ (g)$

3. The mixture of excess carbon monoxide and nickel carbonyl is heated to 220 - 250 °C. On heating the tetra-Carbonyl decomposes to give Ni:

$Ni(CO)_4\ (g) \rightarrow Ni\ (s) + 4\ CO\ (g)$

This chemistry may be very useful for extracting the large amount of Ni present in several systems without the expense of pyrometallurgical operation. The Ni produced is of high purity and suitable for battery manufacturing. A schematic of the process is shown in the following figure. Non – Ni materials, i.e. packaging, would be sent to secondary recovery and possibly the hydrometallurgical system for recovery of other non ferrous metals.

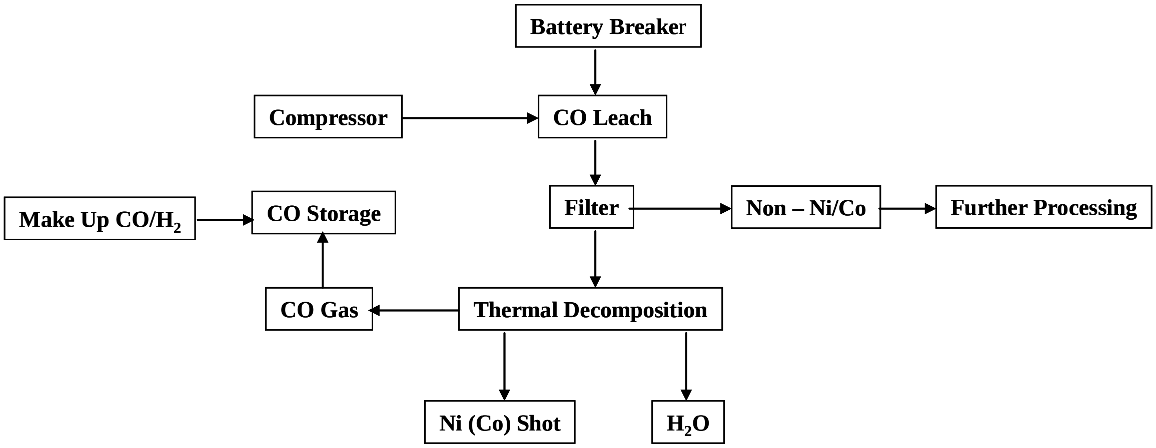


Figure 9: Flowsheet for Recovery of Ni by the Mond Process

Cryomilling:

Toxco recycles Li based cells in their facility at Trail BC. In this process the batteries are broken at -198C (-325F, 74K) with the addition of NaOH which converts all Li metal to LiOH. The addition of carbonate species, i.e. CO_3^{-2} converts LiOH to $LiCO_3$ which is easily handled. Cryomilling reduces the chemical activity of the Li materials as chemical reactivity is proportion to the Exp(1/T) where T = Temperature in K. The highly basic nature of NaOH will form an alkali metal salt with the orgainic carbonates to form glycols. After milling, the electrochemically active materials, i.e $LiCoO_2$ and Li_2CO_3 are separated from plastics and separators by washing on jigging tables. Li compounds and reclaimed plastics are sold to the market. The mixed $LiCO_3$/$LiCoO_2$ material is washed from the packaging scrap, dried and sold as a cake back to the industry. The packaging material is then processed to recover recyclable plastics or sent to a landfill for disposal.

Hydrometallurgy for Battery Recycling:

There are several advantages of recycling batteries using hydrometallurgy. Some of them are the high percentage recovery of valuable metals, ability and flexibility to separate and recover each component, purity of the product obtained, reduced specific energy requirement, high energy efficiency and no air emissions. The versatility of hydrometallurgical processing also allows different types of batteries to be treated with slight modification of the process. An additional advantage of hydrometallurgy is that some of the reagents such as H_2SO_4 and Na_2SO_4 that would likely be used are typically produced in-house during recycling of lead-acid batteries. The main disadvantage of using hydrometallurgy is the high volumes of the process solutions and effluents to be treated.

Ni-MH

The Ni-MH batteries consist of Ni, Co and other RE elements. The positive electrodes are made of a porous Ni plate and $Ni(OH)_2$ as the activating agent. The negative electrodes are made of a porous Ni plate and a hydrogen storage alloy such as Mm-Ni-Co intermetallic. The typical composition of a Ni-MH battery is given in Table12.

Table 12. Chemical composition of Ni-MH Battery electrodes (Yoshida et al, 1995)

	Weight Percent									
Electrode	**Ni**	**Co**	**Mn**	**La**	**Ce**	**Pr**	**Nd**	**Al**	**Zn**	**Fe**
Positive										
(1)	62.4	7.0							0.28	0.01
(2)	62.2	7.1							0.28	0.01
Negative										
(1)	61.3	7.8	3.8	7.3	11.6	0.9	3.7	1.4	0.80	0.10
(2)	67.1	6.9	3.3	6.2	9.9	0.8	3.3	1.2	0.80	0.10

All the elements in a Ni-MH battery can be leached using sulfuric or hydrochloric acid. Rare earth elements can be precipitated with sodium sulfate as $RE\ (SO_4)_2Na.2H_2O$ and treated using an existing rare earth recovery process to separate each element. Solvent extraction at pH 2-3 using DP8R (Di-2-ethylhexyl phosphoric acid) can be used to separate Cu, Zn and Cd followed by electrowinning to recover Ni and Co. The hydrometallurgical process to recycle Ni-MH batteries is given in Figure 6.

Nan et al. (2006) have recently developed a process that includes dissolving the residues with 3M H_2SO_4 at 70 C, separating the rare earths and impurities and then synthesizing spherical $Ni(OH)_2$. Kuzuya et al. (2003) also developed a sulfuric acid leach for the recovery of metal values from Ni-MH batteries. They separated Misch metal, $MmNi_{(5-x)}Co_x$ from the electrode materials by sedimentation and leached it with sulfuric acid. The RE metals dissolved rapidly while Ni leached more slowly. Kleinsorgen et al. (2000) leached the residue containing metal values from Ni-MH cells with H_2SO_4 and H_2O_2. The rare earths were recovered as Na-RE double salts, Fe and Al were precipitated by pH control, and Co and Ni were extracted with DEHPA followed by electrolysis.

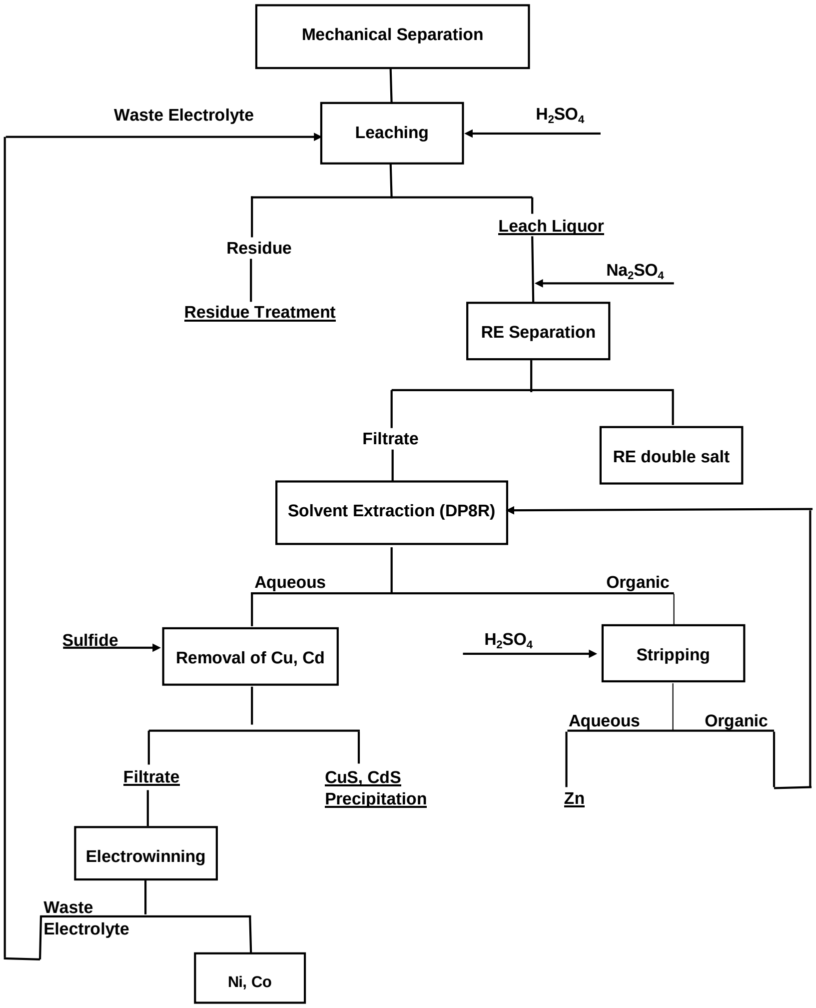


Figure 10. Conceptual Hydrometallurgical Flowsheet to Recycle Ni-MH Batteries (Yoshida et al., 1995)

Pietrelli et al. (2002) leached the residue from Ni-MH batteries with 2M H_2SO_4 and recovered RE as Na-RE double salts. Zhang et al. (1998) leached spent Ni-MH cells using HCl, extracted RE using DEHPA, separated Co from Ni by solvent extraction using trioctyl-amine (TOA). Zhang et al. (1999) also used bis-(2,4,4-tri-methyl-pentyl) phosphonic acid (Cyanex 272) as an extractant to separate Co and Ni with recoveries greater than 98% for each metal. Lupi and Pilone (2002) developed a process in which high purity Co-Ni alloy was obtained by electrowinning with recovery rates greater than 90%.

Ni-Cd

The chemical composition of the electrodes and the active material of Ni-Cd batteries are given in Table 13. Ni is present as metallic nickel and as $Ni(OH)_2$.

Table 13. Chemical composition of Ni-Cd battery constituents (Pietrelli et. al)

	Weight Percent					
Electrode	**Ni**	**Cd**	**Co**	**Fe**	**C**	**SS**
Active Material	28.9	30.70	0.08	0.69	21.60	18.10
Anode	21.80	51.90	0.00	0.02	10.10	16.20
Cathode	26.40	19.80	0.02	0.005	34.00	19.80

The hydrometallurgical process for recycling Ni-Cd batteries is based on leaching with sulfuric acid followed by metals recovery and separation using ion exchange. More than 80% of the metals values dissolved in 1.8 M H_2SO_4 at 110 C (Pietrelli et al., 2001). Cd was separated from Ni at pH 3-4 (separation factor > 10) using the Na-Amino-methyl-phosphonic acid functional group. Residual Fe was precipitated at pH 4. The process layout of the hydrometallurgical process to recycle Ni-Cd batteries is given in Figure 7.

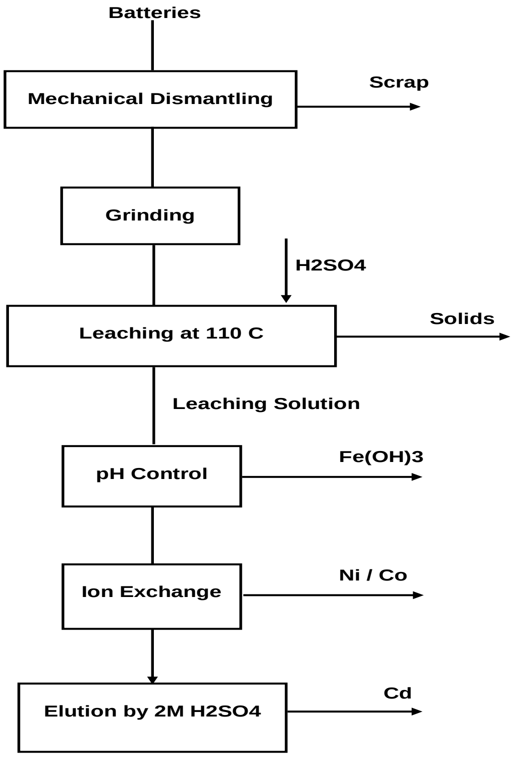


Figure 11. Hydrometallurgical Flowsheet to Recycle Ni-Cd Batteries
(Pietrelli et al., 2001)

Hydrometallurgy of Li-Ion

The powder from battery crushing operation primarily contains $LiCoO_2$. Sohn et al. (2006) leached this residue with 2M H_2SO_4 and 10% H_2O_2 at 75 ^oC with extraction greater than 95% for Li, Co and other metals. Leaching with 3M

Oxalic at 80 ^oC was very selective for Li. More than 99% of the Li was dissolved while only less than 1% Co was leached. In H_2SO_4 + 10% H_2O_2 leach, Co was recovered as cobalt hydroxide or cobalt oxalate which was then converted to cobalt oxide by heat treatment. Li was recovered from the solution as Li_2Co_3 by adding Na_2CO_3. The process to recycle Li-Ion batteries is illustrated in Figure 8.

Contestabile et al. (2001) leached $LiCoO_2$ using HCl followed by cobalt hydroxide precipitation. Zhang et al. (1998) also used HCl for leaching $LiCoO_2$ followed by solvent extraction of Co with PC-88A and precipitation of Co as $CoSO_4$ and Li as $LiCO_3$.

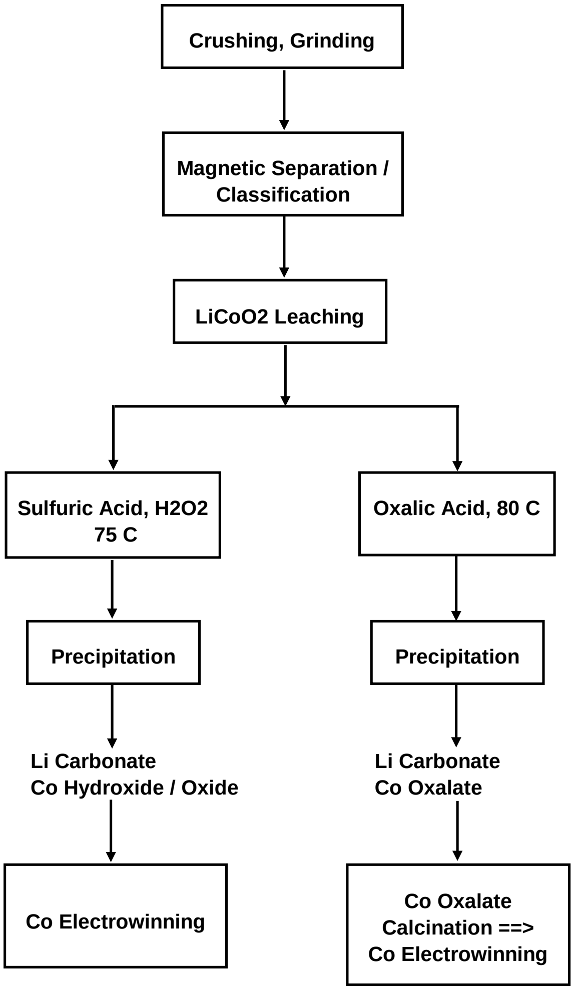


Figure 12. Reconstructed flowsheet to recycle Li-Ion batteries.
(Sohn et al., 2006)

Hydrometallurgy of Zn Alkaline Batteries

Primary Zn is currently produced hydrometallurgically by dissolving ZnO (obtained by roasting ZnS) in dilute H_2SO_4 followed by electrowinning. Not surprisingly, the hydrometallurgical process used to recycle Zn-alkaline batteries also consists of leaching with H_2SO_4.

The anode in alkaline batteries is made of powdered Zn and the cathode is made of MnO_2 and carbon/graphite. After crushing, magnetic separation and sieving, the material to be leached consists mostly of ZnO and MnO_2. This material is leached with dilute sulfuric acid to obtain selective dissolution of Zn with up to 100% extraction efficiency (deSouza and Tenorio, 2000). MnO_2 is soluble in sulfuric acid only at high concentrations.

Frank et al. (1984) developed a process in which the residues from the cells were treated by alkali followed by acids. Zinc and MnO_2 were obtained by electrolysis. Calu et al. (1985, 1986) patented processes in which the batteries were leached with Hydrochloric acid. MnO_2 and graphite were separated and a solution containing heavy metals (Zn, Mn, Hg, Cd, Cu, etc.) was treated for recovery of the metal values. Aoki's process (1986) consists of leaching with sulfuric acid followed by precipitation of Fe and Cu. Electrowinning was used to recover Zn. Other processes also involve acid leaching followed by metals recovery (26-28).

In the BATENUS process (29), several types of batteries are sorted and cryogenically treated prior to crushing them. The powdered material from crushing is leached with sulfuric acid and the metal values recovered by electrowinning and electrodialysis. The whole operation is in a nearly closed reagent cycle and effluent emissions are greatly minimized.

Co-production of Zinc and Manganese Oxide by Electrolysis from a Hydrometallurgial Stream:

Investigation of the Pourbaix diagram, Figures 13 & 14, for Zn and Mn indicates the Zn metal and MnO_2 can be produced simultaneously by electrolysis. The outputs from this process, Zn metal and MnO_2 can be directly returned to the manufacture of Zn-C alkaline batteries and Ni and Li primary cells. The co-electrowining of Zn and MnO_2 is outlined in the paper by Binsfield et al. (8) The Zn and Mn were dissolved in a SO_4^- solution at a concentration of 0.77M Zn and 0.3M Mn with 0.22M H_2SO_4 with Gum Arabic (0.65 ml of 0.125g/l). Electrode reactions were as follows:

Cathode:

$Zn^{2+} + 2e^- \rightarrow Zn^0$

Anode:

$2MnSO_4 + 2H_2O \rightarrow H_2SO_4 + MnO_2 + 2H^+ + 2e^-$

Current efficiency for Zn deposition was found to be greater than 90% for Zn between 500-600 A/m^2. Current densities at 600 A/m^2 were found to produce dendrites on the Anode side ($Mn0_2$). Therefore, a current density of 500

A/m^2 is recommended for the co-electrowinning process. Cathode and anode metallurgy was researched with the recommendation that Al be used for cathodes and Pb-1.0%Ag for the anodes.

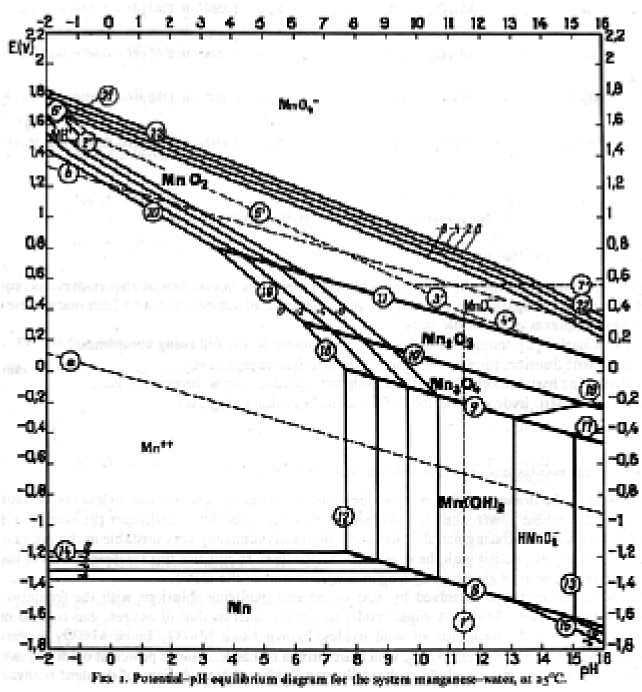


Figure 13: Manganese Pourbaix Diagram

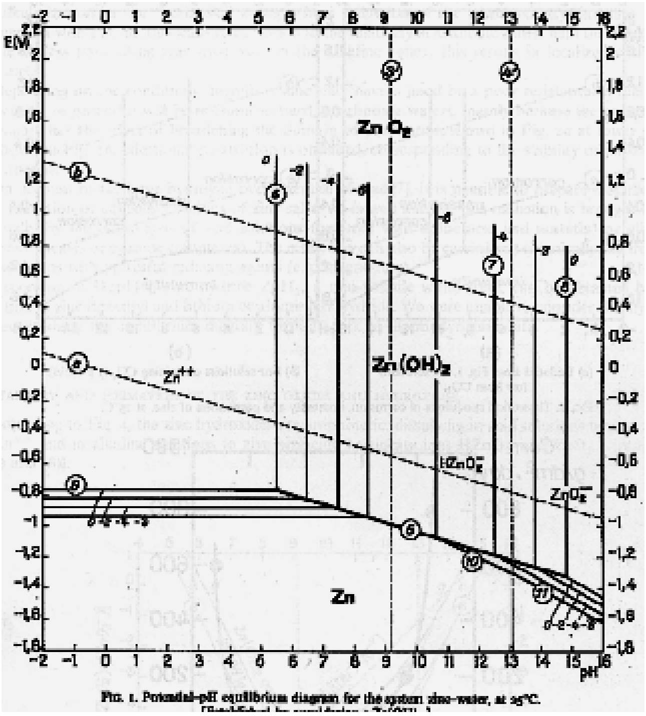


Figure 14: Zinc Pourbaix Diagram

Combined Hydrometallurgical Recycling Process

Most of the non-PbA batteries can be leached with H_2SO_4 with variations of concentration, temperature and additives such as oxidizing agents. The various metals can then be separated by well-established technologies such as ion exchange (Ni, Co), solvent extraction (Ni, Co, Zn), precipitation (Al, Cu, Cd, Fe, Li, Rare-Earths), electrowinning (Co, Ni, Cu), etc.

For hydrometallurgical processing of n-PbA batteries, given the wide range of metals present, it is best to sort the batteries and use a flowsheet specially developed for a particular type of battery. However, for unsorted, non-PbA batteries, a generalized, hydrometallurgical, process flowsheet is illustrated in Figure 15.

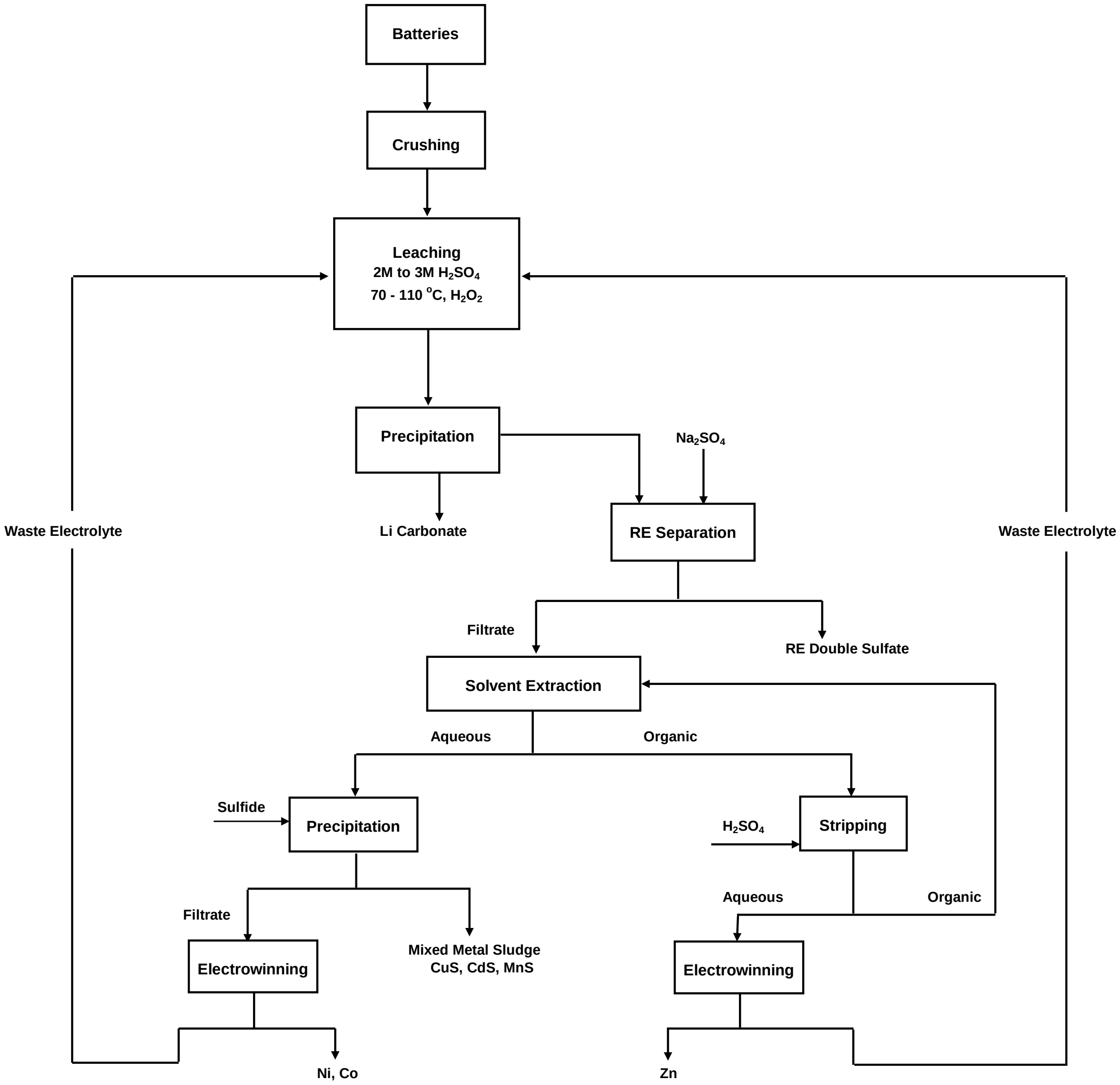


Figure 15. Generalized Hydrometallurgical Flowsheet to Recycle non-PbA Batteries

Recommended Flow Sheet:

Summing the results of our investigation a conceptual recycling flow sheet is now proposed. The criteria for development of this conceptual flowsheet were:

1) Handle a wide range of post consumer batteries, e.g. Alkali, Nickel-Metal Hydride, Lithium Ion
2) Recycling battery grade material as battery grade material preserving a high value product
3) A high degree of intrinsic safety designed into the processes chosen
4) Processes derived from demonstrated technology
5) Minimization of Capital Expense while allowing scalability

To meet the goals presorting the recycled battery stream allows for the segregation of chemistries to enhance safety, e.g. Li ion, improve process efficiency, i.e. eliminate over-treating and WIP and minimize cross contamination. Therefore, it is recommended that acquiring a sorting system be the first technical priority. The sorting system providing a high quality feed to primary recovery operations allows for selecting process which best fit the various chemical systems which have been identified as three (3) general chemistries: Zn/MnO_2, Ni (Ni-MH, Ni-Cd) and Li ion. Best alternative process will also be identified if the proposed processes prove unacceptable for unidentified or foreseen requirements.

Sorting System:

Convention size sensitive sort equipment appear amenible to sorting battery by size, e.g. AAA, AA, D, C. Sorting by chemistry is more challenging. A literature search has indicated that eddy current detection is effective, however, some technique development is deemed appropriate in addition to integration with the physical sorting system.

Zn/MnO_2:

The recovery flow for Zn/MnO_2 either as C or Alkaline cells is conventional hydrometallurgical leaching followed by electrowinning to recover high quality Zn metal and MnO_2 for reuse in battery manufacturing. Conventional pyrometallurgical carbothermic reduction and distillation of Zn away from MnO_x is the preferred alternative.

Ni-Metal Hydride:

In a deviation from conventional Ni metallurgy the Mond process, i.e. carboxylation, is well positioned to remove Ni with high efficiency from battery waste. This process does have unique E, S & H requirements and consideration. However its advantages in a simple flow sheet and the ability to produce high purity material are decided advantages. Alternatively a hydrometallurgical route with electrowinning would allow for recycling of these batteries to be combined with Zn/MnO_2 reprocessing.

Li Ion:

Li ion systems have unique safety requirements in recycling. Specifically the electrolyte used in these cells presents a safety hazard with respect to reactivity and flammability. To perform this task the OnTo Technologies CO_2 extraction process allow for high efficiency separation while mitigating the hazards associated with the electrolyte. The alternative solution is to process these materials with the other cells being recycled hydrometallurgically essentially mitigating the safety hazard by diluting these cells in the overall material flow. In particular special consideration into the design and operation of the battery breaker are necessary.

A simple schematic is now presented to give a visualization of the unit operations and the products to be expected for the proposed flow sheet. Although further matching of the market volumes and economics are necessary preliminary discussions has indicated that these process represent an opportunity to address the market and evolve in capacity and capability as time progresses.

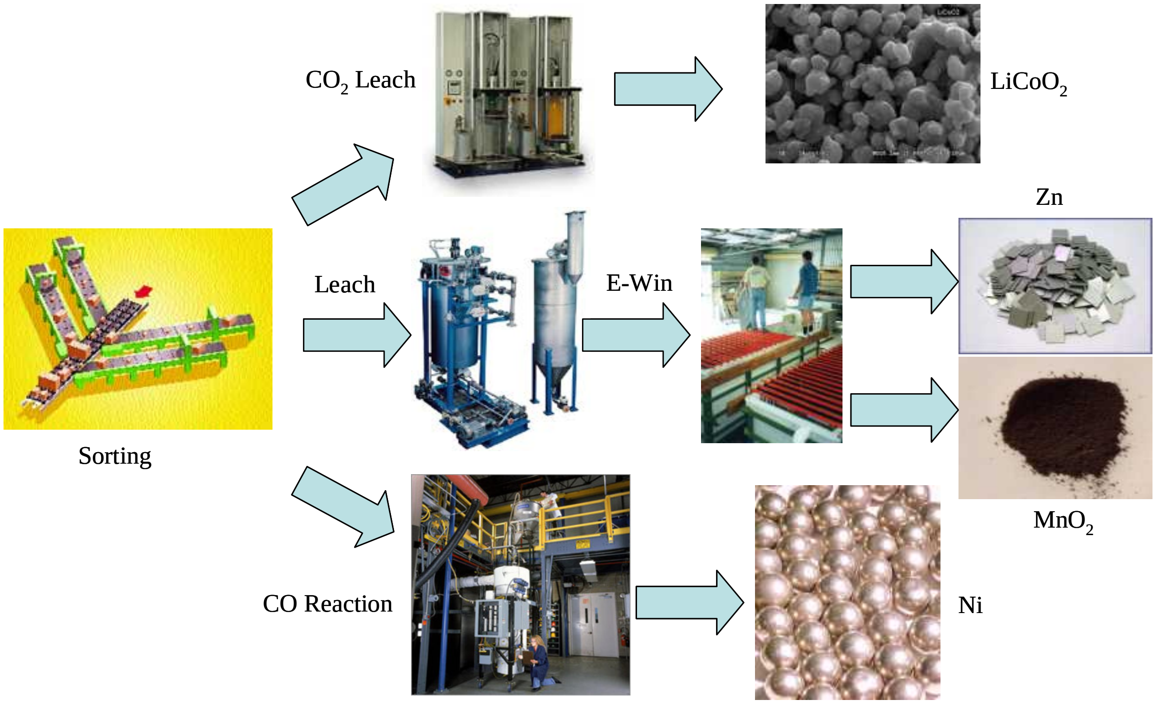


Figure 16: Schematic of proposed Flowsheet and Products

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Appendix I: Structure and Reaction Formula of Batteries (Battery Association of Japan)

Batteries are structured according to type. Here we show the contents of various batteries, which is something you cannot normally see.

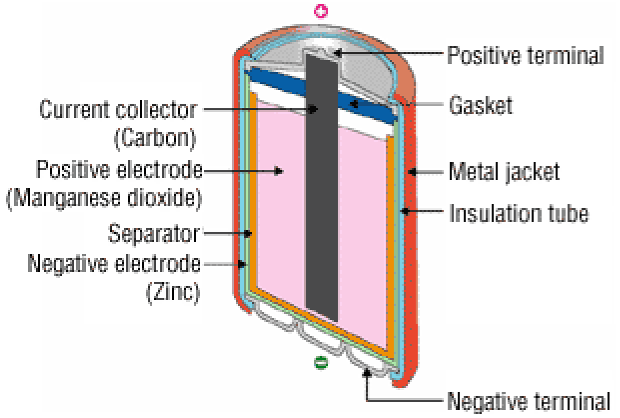

Figure 1: Zinc-Carbon (1.5V), $8MnO_2 + 8H_2O + ZnCl_2 + 4Zn \rightarrow 8MnOOH + ZnCl_2{*}4Zn(OH)_2$

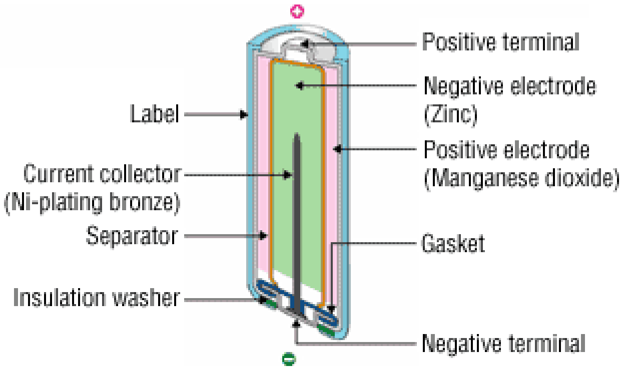

Figure 2: Alkaline-Manganese (1.5V), $MnO_2 + H_2O + Zn \rightarrow Mn(OH)_2 + ZnO$

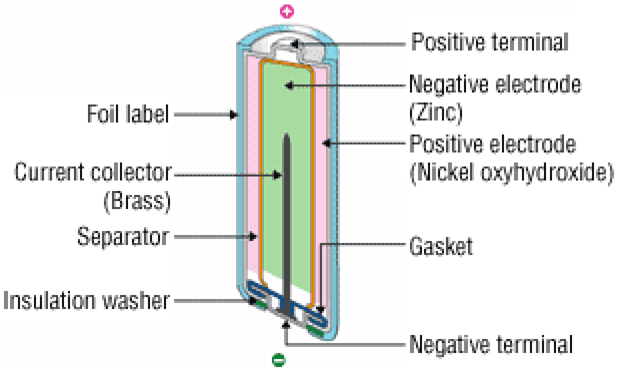

Figure 3: Nickel Primary (1.5V), $NiOOH + MnO_2 + Zn + H_2O \rightarrow Ni(OH)_2 + MnOOH + ZnO$

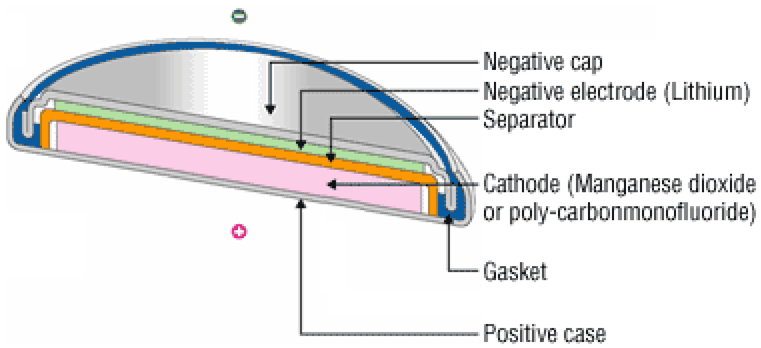

Figure 4: Lithium Primary (3.0V), $\mathrm{Mn(IV)O_2 + Li \rightarrow (Li+)\ Mn(III)O_2}$

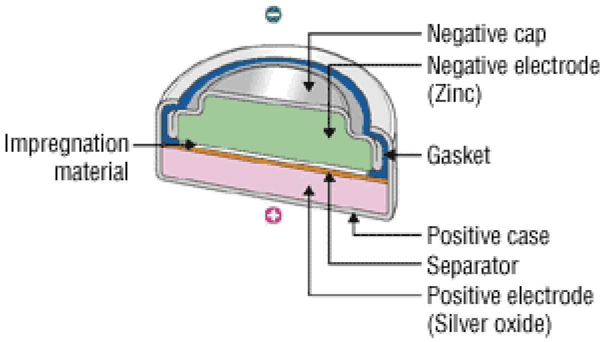

Figure 5: Silver Oxide-Zinc (1.55V), $\mathrm{Ag_2O + Zn \rightarrow 2Ag + ZnO}$

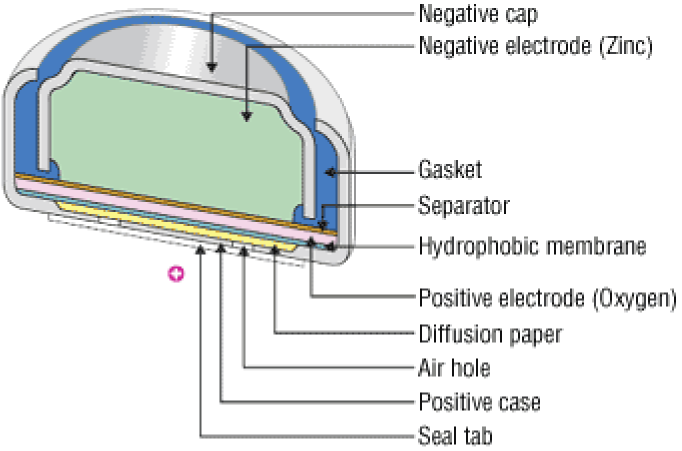

Figure 6: Zinc-Air (1.4V), $\mathrm{0.5O_2 + Zn \rightarrow ZnO}$

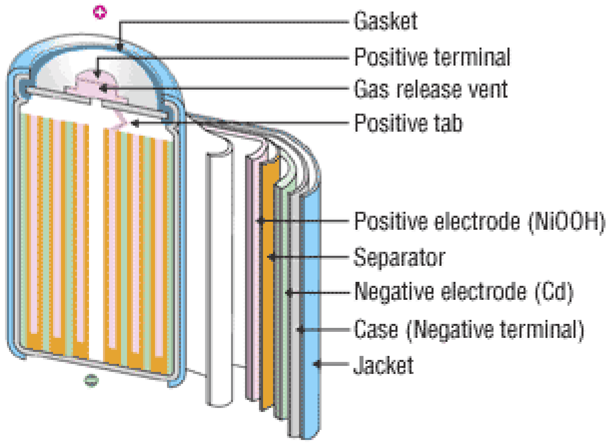

Figure 7: Nickel-Cadmium (1.2V), $2NiOOH + Cd + 2H_2O \rightarrow 2Ni(OH)_2 + Cd(OH)_2$

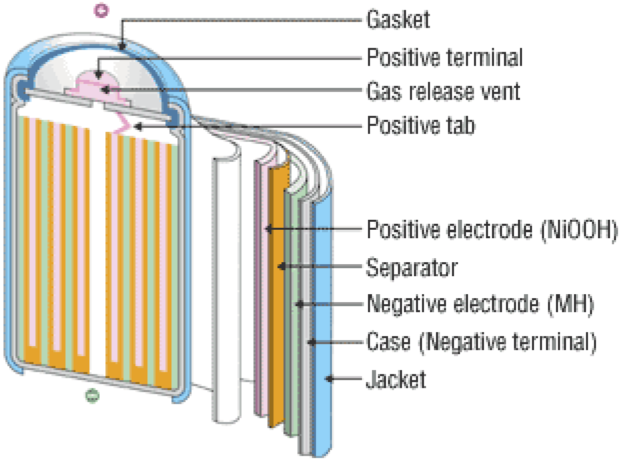

Figure 8: Nickel-Metal Hydride (1.2V), $NiOOH + LaNi_5(H) \rightarrow Ni(OH)_2 + LaNi_5$

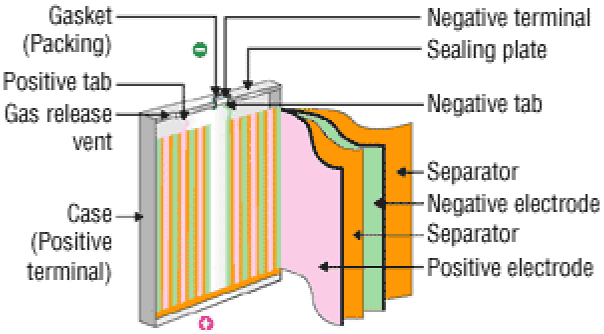

Figure 9: Lithium Ion (3.7V), Li(1-X)CoO2 + Li_xC

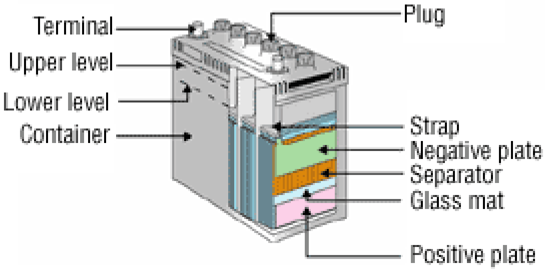

Figure 10: Lead-Acid (2.0V), $PbO_2 + Pb + H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$