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Research Article

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Study of Needed Conditions to Recover the Metal Elements From Spent Batteries (Zn-C) By Hydromettalurgical Method

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Abstract In this research, we study the operation of recovering Zn and Mn elements out of spent batteries (Zn-C). The operation is done with Hydrometallurgy by deposition in the form of Sulphides depending on the values of Ksp of the studied elements components. The batteries (Zn-C) were cut into slim slices, then mixed, and milled. The outcome was exposed to electrical magnet to detach the external iron cover. The remained batteries were sifted to allow the black powder, which comprises (Carbon-the dissolved Zinc from the Zinc case into the paste-the Manganese oxide hydroxide), to pass through. The pieces of Zinc cover and the Plastic pieces were stuck on the sieve, then the Plastic pieces were detached from the Zinc cover pieces by flotation. The Zinc cover pieces were then treated with Hydrochloric acid HCl (2N) to form Zinc chloride solution which is treated with Ammonium sulphide $(NH_4)_2S$ and Zinc Sulfide was precipitate. The remains were detached, washed and dried, then the powder was treated with distilled water to dissolve the complex Zinc compounds to precipitate them in the form of Zinc Sulfide ZnS. Then, the remained paste was treated with Citric acid ($C_6H_8O_7$) so the Manganese compounds were dissolved and formed complex compounds from which the Manganese is recovered by precipitate it on the form of Manganese Sulfide MnS by Ammonium sulphide $(NH_4)_2S$. The final remained unreacted substance which is Carbon was separated and dried until weight is constant.

The research benefits the environment to get rid of Batteries' wastes and in economically to recover the studied elements Zn, Mn in addition to side outputs (Iron, Plastic and Carbon).

Keywords recover metal elements, spent batteries (Zn-C), Hydrometallurgy, Pyrometallurgy, Zinc, Manganese

Introduction

As a result of the increasing scientific and technological development day by day and the increase in the number of electronic devices of different types, the number of batteries fed to these devices has increased simultaneously, and it is known that these batteries have a relatively specific age according to the type and use, and therefore they will be spent after a certain period and will turn into solid waste and because of the increased use of electronic devices, the number of spent batteries increases daily, An example of this increasing , this number in Taiwan annually reached 9000-10000 tons annually [1,2]. When dealing with these batteries as regular waste and accumulating in nature without treatment, this will lead to damage to the ecosystem in addition to the animal and plant kingdom and therefore it will cause direct harm to the human being due to its transmission to it through the food chain. If these batteries are recovered, this will reduce the harmful effect on environment in terms of disposal of these wastes and the mitigation of toxic emissions and harmful pollutants during the extraction and industrialization processes, and

also these elements will constitute an important economic resource as they are extracted from natural raw materials that are constantly depleted and are non-renewable resources. It also leads to an abundance of production costs, because the cost of recovering it is less than the cost of extracting it from its natural materials [3,4,5]. It has been observed in recent years that the global interest in battery recycling processes of various types has increased. In 2009, the rate of recycling of (Zn-C) batteries in Taiwan reached 50%, and this ratio is equivalent to the rate of recovery in Europe in the same year, according to a Statistical study of the Taiwan Recycling Organization Council also In Germany, it sells 32,400 tons of batteries annually. In the same year, GRS organization managed to collect 15,000 tons of these batteries for recycling [1,6].
Hence the tendency in this research was to recover metal elements from various damaged batteries.

Research Methods and Materials

Pyro metallurgical Method

A method used to extract minerals from its ores using heat treatment, these includes smelting, roasting, transforming and refining operations [7].

Hydrometallurgical Method

A method used to extract minerals from its ores using acids and bases treatment by dissolving operations, it includes different chemical reactions in these solutions to obtain the minerals [7].

Research objectives and importance

The aims of research lies in several mail points, as follows:

1- Recover the mineral elements from the spent batteries (Zn-C) by precipitate them as sulfides.
2- Use the Hydrometallurgical method to recover minerals element, as its distinguished from Pyro metallurgical method as being less expensive and not harmful.
3- Take advantage in economy and industry from the recovered minerals element.
4- Dispose of spent batteries that negatively affect the environment and the human being.

Experimental Work

Chemicals and devices used in research

The chemicals were used in work are shown in the table 1.

Table 1: List of chemicals used

Material	Chemical formula	Molecular weight	Density	Purity	Company
Hydrochloric acid	HCl	36.46	1.19 g/cm^3	37 %	POCH
Citric acid ,monohydrate ,pure	$C_6H_8O_7.H_2O$	210.14	-	99 %	HIMEDIA
Ammonium poly sulphide solution	$(NH_4)_2S$	**68.094**	**-**	20 %	BDH

Devices and tools were used

1- Sensitive electronic balance (brand: Santorus)
2- Heater and magnetic drive (brand: Yellow line)
3- Electric saw (brand: Makita)
4- Porcelain grill and metal crusher
5- Normal metal cutter

Sampling

Batteries are electrical devices that contain chemicals which provide electrical energy of various capacities through chemical reactions including, depending on the type, strength and sustainability of chemical reactions taking place and chemicals involved in manufacturing. These batteries are the most wide spread in simple household appliances and consist of a positive electrode (Carbon rod) and a negative electrode (Zinc) and surrounded by a paste of Ammonium Chloride, according to the manufacturer, And the paste is surrounded by a thin paper cover then, it is covered with a metal Zinc coating followed by a thin layer of Plastic for protection. Then the external metal casing. The resulting energy is connected through two poles: the upper positive electrode and the bottom positive electrode, these batteries are not rechargeable [8,9]. The experimental work was done on the dry battery (Zn-C) also known as ($Zn\text{-}MnO_2$) batteries, where the necessary samples were collected to carry out the study and it was obtained from a landfill and from household waste, some of which were purchased new and the process of discharging them from electricity using a light bulb until extinguishing and thus we get a spent batteries and table 2 shows types of batteries which were used in the practical study, its natural condition, brand and country of manufacture .

Table 2: The type of batteries, its natural condition, brand, and country of manufacture which were used in the practical study

Battery kind	Brand	Status	Country	Number
Zn-C	Panasonic	dry	JAPAN	**5**
Zn-C	TOSHIBA	dry	TAIWAN	**5**

In Figure 1 and Figure 2, the internal content of the spent (Zn-C) battery are shown.

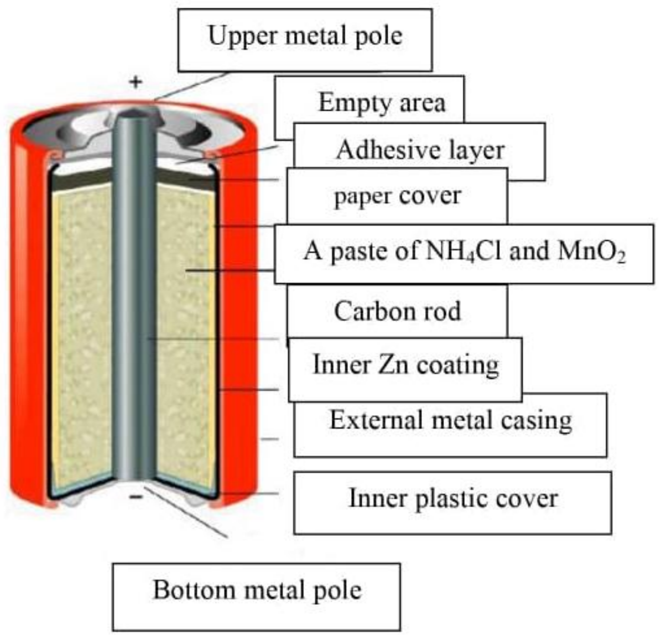

Figure 1: Detailed section of components and parts of this battery

Figure 2: The internal content of the spent (Zn-C) battery

In Figure (1) shows a detailed section of the components and parts of this battery After the battery is spent, the external metal casing will be exposed to rust Likewise, a large part of inner Zinc coating will be oxidized toward the inner paste and the battery will swell Figure (2) shows the dry battery content after its damage.

Study Methods

Separation scheme for consumables of (Zn–C) batteries type D

Then the process of separating the components of the batteries and recovering the metal elements as follows:

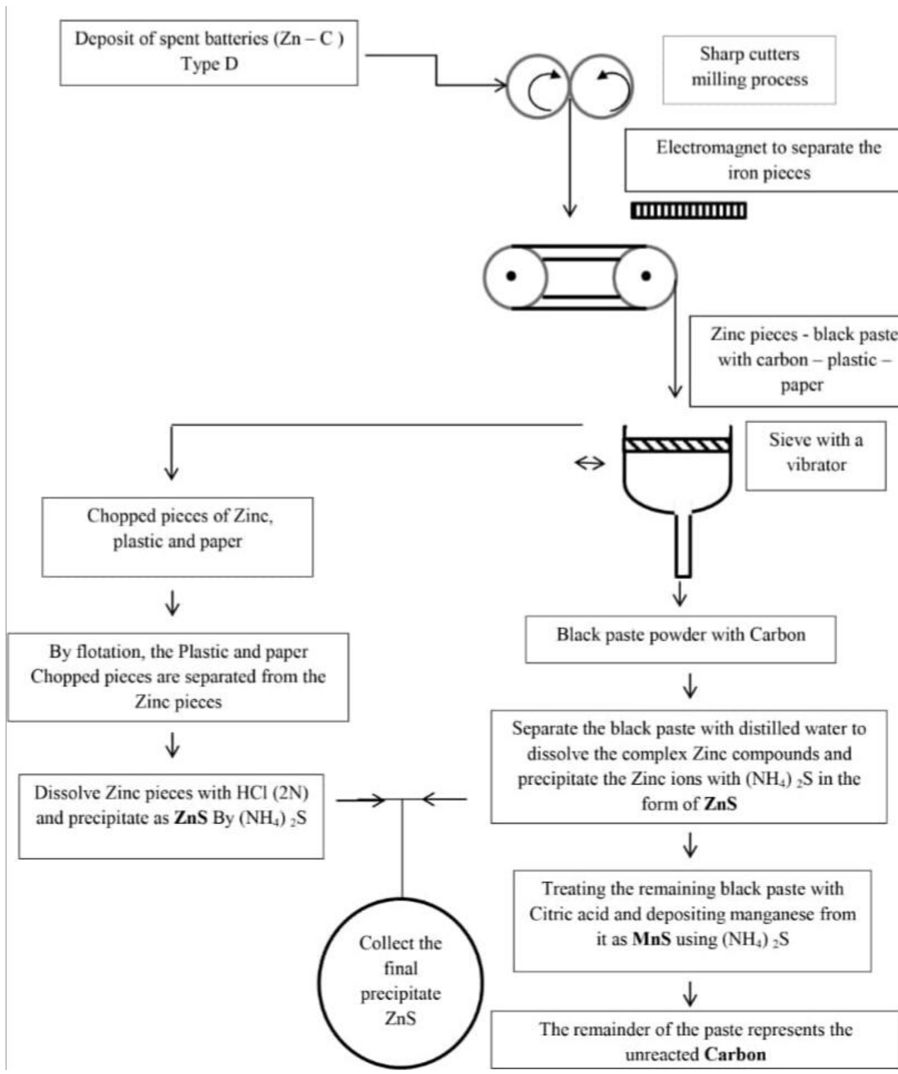

Figure 3

1- Separate the iron pieces from the external casing and from poles of the (Zn-C) Battery:

The separation of the iron pieces from the external casing of the battery and from poles is carried out by using Electromagnet that pulls all the metal parts.

2- Separating the Zinc and plastic parts and paper Pisces:

The Zinc, Plastic and Paper Pisces are separated from paste and Carbon mixture using a suitable sieve.

3- Separate the Zinc pieces from the plastic and paper pieces:

The separation process is done by flotation, as the plastic and paper float the Zinc parts fall down to the bottom.

4 - Zinc recovery: There are two sources of Zinc:

First source (Battery inner coating):

Zinc was Recovered from the inner casing of the battery by using Hydrochloric acid HCl (2N) after adjusting and specifying optimal conditions for recovery from: temperature, moving speed, contact time, mixing ratio, liquid: solid, medium pH

Then by participating with Ammonium Sulfide $(NH_4)_2S$ in the form of ZnS.

The second source (the Zinc oxidized that is transferred to the paste):

The Zinc was Separated from the black paste by distilled water by dissolving the complex Zinc compounds and precipitate the Zinc ions with Ammonium Sulfide $(NH_4)_2S$ in the form of ZnS, and then we collected ZnS from the two mentioned sources.

5- Recover Manganese from black paste:

After the process of recovering Zinc from the paste, Manganese was recovered by using Citric acid after tests were conducted to ensure that the Carbon in the paste would not interact with Citric acid. The recovery process was carried out under optimal conditions of: temperature, Stirring speed, Stirring Time, Ratio of reactants (liquid: solid) And measure the pH value.

After the process of dissolving the Manganese compounds and obtaining a solution was done, the Manganese was participated by adding Ammonium Sulfide $(NH_4)_2S$ until the complete precipitation where we get a pink precipitate in the skin color Of Manganese sulfide MnS.

Results and Discussion

Study of Zinc recovery from the battery (Zn-C) inner metal casing:

we took a piece of 1 gr of the inner metal casing of the battery and treated with HCl (2N) until completely dissolved, and it consumed an amount of 15 ml of acid, forming a solution containing $ZnCl_2$ due to the reaction:

$Zn + 2HCl \rightarrow ZnCl_2 + H_2$

Then a 20% Ammonium Sulfide solution was added to the Zinc Chloride solution until complete precipitation. Consumed a quantity of 5.3gr of the Ammonium Sulfide solution and the deposition of white Zinc Sulfide according to the reaction:

$ZnCl_2 + (NH_4)_2S \rightarrow ZnS\downarrow + 2NH_4Cl$

After the digestion process, the precipitate was separated and dried to a constant weight, then measured to 1.48 gr It is the mass of Zinc Sulfide after the process is over

Theoretically calculated percentage of retrieval

$Zn + 2HCl \rightarrow ZnCl_2 + H_2$

65.3 gr 136.3 gr Molecular weight

1 gr X gr Experimental weight

X= 136.3/65.3 = 2.0873 gr

It is the amount of Zinc Chloride in the solution

$ZnCl_2 + (NH_4)_2S \rightarrow ZnS\downarrow + 2NH_4Cl$

136.3 gr 97.365 gr Molecular weight

2.0873 gr Y gr Experimental weight

Y = 97.365 x 2.0873/136.3 = 1.491 gr

It is the theoretical Zinc Sulfide mass

Examining the optimal conditions for recovering Zinc from (Zn-C) battery's inner metal casing:

We note that the rate of recovery of Zinc at a degree of 25 °C reached 93.89%, which is low. Therefore, the optimum conditions were studied in order to raise the rate of recovery. The ratios of the reactive materials and the solution pH were stabilized and the temperature was raised. From the table (3) the best recovery rate is at sample 3. at a temperature of 40 °C, which is the best as a recovery rate and the most economical sample

Table 3: The Examining of the optimal conditions for recovering Zinc from (Zn-C) battery's inner metal casing

The sample number the conditions	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**
ratios of the materials Zn + HCl	1gr : 15 ml	1gr : 15 ml	1gr : 15 ml	1gr : 15 ml	1gr : 15 ml
pH	**9**	**9**	**9**	**9**	**9**
Temperature ℃	**20**	**30**	**40**	**50**	**60**
Stirring speed rpm	**400**	**400**	**400**	**400**	**400**
Stirring time min	120	120	120	120	120
$(NH_4)_2S$ gr Quantity	**5.3**	5.3	**5.3**	**5.3**	**5.3**
Quantity ZnS gr	**1.40**	**1.45**	**1.5**	**1.5**	**1.5**
percentage % recovery	**93.3**	**96.6**	**99.9**	**99.9**	**99.9**

Study of Zinc recovery from black paste

A weight of 4 gr of black paste was taken and treated with 200 ml distilled water at a temperature of 25 ℃ and a contact time of 120 min and Zinc ions were detected using $(NH_4)_2S$. We observe the appearance of a Cloudy White ZnS indicating the presence of Zinc in the filtrate and then filter then We treat the filtrate a second time, as mentioned previously, and detect Zinc ions, so the result was negative, meaning there are no Zinc ions ,We conclude from this that the first treatment was sufficient to obtain Zinc ions from the black paste.

Then, the optimal conditions for recovering Zinc from the black paste were studied. We took the first filtrate and added 1 ml of $(NH_4)_2S$ a white colloidal suspension formed, Zinc Sulfide.

Accordingly, we have studied the ratios, conditions, and ratios of retrieval as shown in Table 4, studying the ideal ratios and conditions of retrieval.

Table 4: The Examining of the optimal conditions for recovering Zinc from (Zn-C) battery's black paste

The sample number the conditions	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**
Weight of sample gr	4	4	4	4
Stirring time min	120	120	120	120
Temperature ℃	15	25	35	40
pH	9	**9**	9	9
Stirring speed rpm	400	400	400	400
Quantity ml $(NH_4)_2S$	1	1	1	1
ZnS gr recovered	0.15	0.25	0.25	0.25
Zn gr recovered	0.10065	0.1716	0.1716	0.1716
percentage % recovery	75	94.4	94.4	94.4

And from it Sample (2) achieves the best recovery rate and the best conditions

Weighting accounts

The weight of the recovered ZnS from the sample was 0.25 gr

	Zn	ZnS
Molecular weight	97.44	65.38
Experimental weight	0.25	**X**

X = 0.1716 gr The amount of Zinc contained in a 4 gr black paste

Discussion of Results

Before use, the battery contains Zinc of 15 gr after the battery was put into use, the amount of Zinc in the casing was 12 g, this means turning 3 gr of Zinc into the paste. Upon completion of the paste treatment process, we recovered a quantity of 2.83 gr. Thus the total amount of Zinc recovered is 14.83 gr out of 15 gr.

Hence the total recovered rate 100 x 14.83/ 15 = 97.33%.

Study to recover Manganese from black paste

We took a sample of 4 gr of paste from the battery used in the previous section, We put with it an amount of Citric acid and 200ml distilled Water then by Exposing it to the heating and stirring operations, Then the sample was presented to the filtration process, and then Ammonium Sulfide was added, and a Pink filtrate appeared containing Manganese, and then we repeated the recovery process several times, as Manganese recovery stopped at the Third stage.

We registered the conditions and percentages related to the experiment. Table 5 shows the conditions and ratios of the initial recovery of a 4 gr paste sample to study the recovery of Manganese

Table 5: The conditions and ratios of the initial recovery of a 4 gr paste sample to study the recovery of Manganese

Conditions and proportions	1st retrieval	2nd retrieval	3rd retrieval	4th retrieval
Distilled water ml	200	200	300	400
℃ Temperature	25 to Boiling	25 to Boiling	25 to Boiling	25 to Boiling
Stirring time min	30	30	30	30
Boiling time min	10	10	10	10
Stirring speed rpm	600	600	**600**	**600**
Weight of Citric acid gr	4	3	2	2
pH	5	2	2	1
Presence of Manganese	+	+	+	-

Examine the optimal conditions for Manganese recovery

Depending on the previous experience, we studied the experiment of recovering Manganese from the spent battery paste using Citric acid, where the study was conducted on a sample 4 gr of paste, the best ratio and conditions for retrieval of the sample were determined, and table 6 shows the process of recovering Manganese From the spent battery paste and the best conditions and recovered ratios.

Table 6: The process of recovering Manganese from the damaged battery paste and the best conditions and recovered ratios

Conditions and proportions	1st stage	2nd stage	3rd stage
Distilled water ml	200	200	200
℃ Temperature	25 to Boiling	25 to Boiling	25 to Boiling
Stirring time min	25	25	25
Boiling time min	10	10	10
Stirring speed rpm	600	600	600
Weight of Citric acid gr	4	3	2
pH	5	3	2
Amount retrieved MnS gr	1.14	0.7	0.23
Amount retrieved Mn gr	0.72	0.44	0.144
Percentage recovery %	53.62	32.76	10.72

And according to the reference [10] the percentage of Manganese in the battery according to XRD is 32.80% on it, the amount of Manganese within 61.44 gr paste is 20.154 gr and the recovered amount: 19.569 gr**.** The overall recovery for Manganese is 97.1%.

Some properties of recovered Sulfides

1-ZnS Zinc Sulfide:

1- One of the most important semi-conductors
2- In optical sensors
3- In the solid layers of solar cell windows as an optical conductor
4- Anti-reflective coating for infrared devices
5- In producing hydrogen [11, 12]

2- Manganese Sulfide MnS:

1- In semiconductor applications
2- In the lithium ion batteries
3- Electrode in super capacitors
4- Emitters (broadcast devices) in green and blue colors
5- Solar energy insulation and protection materials [13, 14]

Interpretation of the results

The low values of The Ksp for the studied element sulfides resulted to a very good precipitation rates and very few losses, in table 7, we show the Ksp of the Sulfites of the studied elements [15].

Table 7: The Ksp values for the Sulfites of the studied elements

Name	Formula	Ksp value
Zinc Sulfide	ZnS	$4.5x10^{-24}$
Manganese Sulfide	MnS	$3x10^{-13}$

Recommendations

1- Use the Hydrometallurgical method to recover the mineral elements contained in the Gel Battery.
2- Using the Hydrometallurgical method to recover the metal elements contained in batteries lithium ions (Li-ion).

Conclusions

1- Zn was recovered from the internal Zinc shell and from the internal paste of the damaged (Zn-C) battery by 97.33%.
2- Mn was recovered from the internal pulp of the damaged (Zn-C) battery by 97.1%
3- Iron metal, carbon and plastic were recovered from the battery (Zn-C) as by-products of recovery operations without loss

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