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Characterization of Spent Household Zinc-Carbon Dry Cell Batteries in the Process of Recovery of Value Metals

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ABSTRACT

Spent zinc-carbon dry cell batteries were characterized to assess the environmental impacts and also, to identify the potentials of recovering the metal values from these batteries. Different component parts of both new and spent batteries of all the five types (AAA, AA, C, D and 9V) were examined. The outer steel casings were found to be tin plated. Steel, zinc and manganese constituted 63 percent of the total weight of the battery. Average zinc and manganese contents were about 22 and 24 percent of the total weight of spent batteries. The electrolyte paste of the spent batteries contained 22 wt. percent zinc and 60 wt. percent manganese. The rest was chlorine, carbon and small amounts of iron and other impurity elements. The major phases in the fresh batteries were carbon, MnO_2 and NH_4Cl, while $Zn(NH_3)_2Cl_2$, $ZnO.Mn_2O_3$, Mn_3O_4 and Mn_2O_3 were the prominent phases in the spent batteries. Presence of mercury and cadmium were not detected and a small percentage of lead was found in both the zinc anode and in the electrolyte paste.

Keywords: *Zinc-carbon battery, Characterization, Spent batteries, Waste management*

1. INTRODUCTION

Zinc-carbon dry cell batteries are widely used in different household applications like toys, radios, recorders, watches, remote controls, cameras, torches etc. These batteries are not rechargeable and are discarded when discharged. Household batteries are, at present, disposed (along with other household solid waste) in municipal solid waste (MSW) and are sent to a landfill or, in some countries, to a municipal waste combustion facility. When disposed in a land fill, the elements of the spent batteries can undergo natural leaching, seep into the ground water, change the water's pH and contaminate it [1]. The incineration of batteries also poses two major potential environmental concerns. The first is the release of metals (Zn, Pb and Hg,

if present) into the ambient air and the second is the concentration of metals in the ashes that must be landfill. The stabilization process on the other hand is a costly process [2].

Zinc-carbon batteries and alkaline dry cell batteries are the most used types of batteries and constitute approximately 80% of waste dry-cell battery stream [3]. In the recent past mercury and cadmium along with lead were the main hazardous components in a zinc-carbon battery. In recent years mercury and cadmium are not used in zinc-carbon and alkaline manganese batteries [4]. However, a small amount of lead is still being used in these batteries.

Ever increasing demand for metals is causing a rapid depletion of the primary metal sources (ores). Extraction of metals from the secondary sources requires less energy, helps preserve natural resources and reduces environmental pollution due to the production processes. Increasing attention is now being focused on the secondary sources and considerable progresses have been made towards the recovery of metal values from various secondary sources that include wastes. Spent dry cell batteries contain significant quantities of useful metals that can be technically extracted and reused [5]. At the same time, the development of a suitable method for the recovery of value metals from spent dry cell batteries can decrease the amount of wastes to be disposed and thus reduce the disposal and treatment problems.

Detailed information on the exact nature and content of metal values and other component parts are useful for the development of a suitable process for the disposal or the utilization of the spent dry cell batteries. This study focuses on the determination of the nature and amount of the different metals in all the commercial types of zinc-carbon batteries so that a suitable process for the extraction of all metal values could be developed.

2. EXPERIMENTAL

Samples of spent batteries of all the five commercially available types of zinc carbon dry cell batteries (AAA, AA, C, D, 9V) were collected from different sources: houses, student residential halls, and local scrap shops as well as from the streets through the street children. A wide range of the zinc carbon dry cell battery brands like Sunlight, Motoma, DQ power, Imperial, Brave, Haque Imperial, Olympic, Olympic gold, Sony, Sony super, National Hyper, Panasonic Hyper, Li Feng, New leader, Everlast, Pako and Standard were found during the collection. The samples, irrespective of the brands, were divided into the different types. Some batteries were too badly damaged for physical separation of the components and were discarded. For the C type batteries, only National Hyper and Panasonic Hyper brand batteries could be collected. Some new batteries of each of the five types were bought to compare with the spent ones.

The samples were dismantled manually and the different component parts were carefully separated and weighed. The weight proportions of the different components (casing, paste, etc.) of ten samples in each type of both new and spent battery were estimated. The proportions of the different components reported in this presentation are the average of the values determined on ten samples. The compositions of the electrolyte paste in both new and spent dry

cell batteries were determined by Rigaku X-ray fluorescence (XRF) spectroscopy machine, and the phases present in the paste were identified by X-ray diffraction (XRD) analysis. The XRD pattern was recorded in Panalytical X-Pert diffractometer using Cu K_α (λ=1.54056 A^o) radiation.

The amount of zinc oxide in the anode was estimated by chemical analysis [5**].** Around 5g of the anode zinc of both the new and the spent battery were first dissolved in ammoniacal ammonium chloride (Muspratt) solution under constant stirring for one hour at 50^0C. Zinc oxide of the anode dissolves in this solution while the metallic zinc portion remains undissolved. EDTA complexometric analysis with Erichrome black T indicator was done to determine the zinc content in the solution, which consequently gave the estimation of zinc oxide in anode.

For the determination of moisture content, a 20g sample of the electrolyte paste was heated in an oven at 110^0C to a constant weight. The difference in weight of the as received and the dried sample was used to determine the moisture content of the electrolyte paste.

3. RESULTS AND DISCUSSION

3.1. Identification of the Structural Components

Samples of dry cell batteries (both new and spent) were dismantled manually and the different parts were identified. A dismantled C type battery with its different component parts is shown in Fig. 1.

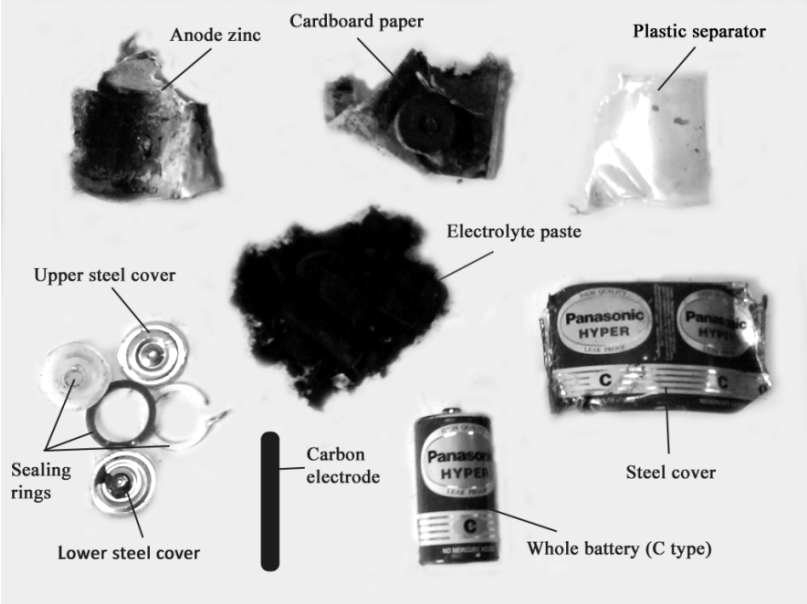

Fig. 1: A dismantled C-type zinc-carbon dry cell battery

The steel plate in the battery was found to be tin-plated. This finding agrees well with the results obtained by others [6]. The existence of tin in the steel was detected by X-ray fluorescence (XRF) analysis (Table 1).

Table 1: XRF analysis of steel casing of a D type new zinc carbon battery

Elements	Na	Si	S	Cl	Cr	Mn	**Fe**	Ni	Cu	**Sn**
Wt %	0.0738	0.038	0.014	0.025	0.0343	0.355	**98.71**	0.035	0.056	**0.652**

3.2. Estimation of Zinc and Zinc Oxide on Anode

In the new and spent batteries, zinc oxide was found to be 7.65% and 58.34% respectively of the total weight of anode. The amount of zinc oxide is clearly more in the spent batteries and this may be attributed to the oxidation of the anode during discharging reactions in the battery. Moreover, wide variation in the amount of zinc oxide was observed due to the different condition of the batteries when discarded.

3.3. Moisture Content Determination

The moisture content in the electrolyte paste of the spent batteries, as determined by heating to constant weight, was found to be 12.32%. This value agrees well with the results (11.2%) obtained by other investigators [7].

3.4 Estimation of Carbon, Hydrogen and Nitrogen in Electrolyte Paste

Carbon, hydrogen and nitrogen were determined in EuroEA Elemental Analyzer. In each case three samples of electrolyte paste was analysed and the results presented are the average values. Both the new and spent batteries were analyzed and the total amount of carbon, hydrogen and nitrogen in both the types were almost identical. Ammonium chloride dissociation is a spontaneous reaction in presence of water. The analysis was done on a dry basis. The evaporation of moisture and the dissociation of ammonium chloride in presence of atmospheric moisture might have yielded the same total amounts in both the new and spent batteries. The analysis result is shown in Table 2.

Table 2: Elemental analysis for the determination of C, H and N (On dry basis)

New types (AA type)					**Spent types**				
No.	**C%**	**H%**	**N%**	**Total**	**No.**	**C%**	**H%**	**N%**	**Total**
1	4.135	0.4175	0.598	**5.44%**	1	4.248	0.458	0.681	**5.43%**
2	3.913	0.38	0.587		2	5.004	0.391	0.724	
3	5.038	0.485	0.758		3	4.369	0.384	0.555	
Average	**4.362**	**0.428**	**0.648**		**Average**	**4.370**	**0.411**	**0.653**	

3.4. Weight Percentage Analysis

Table 3 gives a comparison of the weight proportions of different component parts in spent and new batteries. A variation in the proportions of zinc anode and the electrolyte paste in the new and spent zinc carbon dry cell batteries were noted. This may be attributed to the gradual corrosion of the anode zinc which move to the electrolyte paste during the discharge of the batteries and consequently, change the proportion. However, no significant variations in the proportions of the carbon electrode or of the other parts of the new and the spent batteries could be detected.

Table 3: Wt. % comparison of different component parts in five type new and spent batteries

Components	AAA type		AA type		C type		D type		9V type	
	New (%)	Spent (%)	New (%)	Spent (%)	New (%)	Spent (%)	New (%)	Spent (%)	New (%)	Spent (%)
Whole battery	100	100	100	100	100	100	100	100	100	100
Steel casing	-	-	17.83	17.47	13.97	14.00	11.73	11.08	16.79	16.65
Polyethylene	1.39	1.48	1.21	1.08	0.90	0.88	0.48	0.69	1.30	1.30
Zinc casing	**34.44**	**29.44**	**22.14**	**16.98**	**17.19**	**15.54**	**16.68**	**13.69**	**8.32**	**6.45**
Upper steel plate (1)	1.28	1.16	1.27	1.26	1.87	1.93	1.40	1.43	7.60	6.50
Upper steel plate (2)	-	-	-	-	-	-	0.25	0.34	-	-
Lower steel plate	1.53	1.54	1.04	1.23	1.48	1.57	1.31	1.17	-	-
Cardboard paper	4.72	4.70	9.83	9.66	3.29	2.67	6.12	6.01	12.47*	12.52*
Sealing rings					1.83	1.607	0.11	0.08	-	-
Electrolyte paste	**45.56**	**47.65**	**39.97**	**42.97**	**53.55**	**54.68**	**54.76**	**59.24**	**52.01**	**55.56**
Carbon electrode	**7.64**	**7.46**	**6.10**	**6.12**	**5.55**	**5.51**	**5.71**	**5.54**	-	-
Loss	3.44	6.57	0.63	3.22	0.37	1.613	1.46	0.71	1.51	1.023

3.5. Characterization of the Anode

Table 4: XRF analysis of the new and spent D type battery anode

No	Component	Result	
		New anode	Spent anode
1	Mg	0.0548	0.0647
2	Al	0.0991	0.212
3	Si	0.263	0.391
4	P	0.0232	0.118
5	S	0.0252	0.0393
6	Cl	1.01	2.17
7	K	0.0439	0.0507
8	Ca	0.0659	0.0785
9	Mn	0.0352	0.0626
10	Fe	0.0353	0.114
11	Ni	0.0066	0.0070
12	Cu	0.0102	-
13	**Zn**	**98.0**	**96.2**
14	Pb	0.363	0.459

The composition of the zinc anode, as determined by the x-ray fluorescence (XRF) analysis, is given in Table 4. In the dry cell batteries high purity zinc (purity over 99%) is used as anode material [8]. In a new and spent D-type battery, the purity was found generally 98% and 96.2%. Correction to exclude chlorine that comes from the electrolyte paste and silicon, which is an extraneous impurity, gives the purity figures as 99.27% and 98.76% respectively.

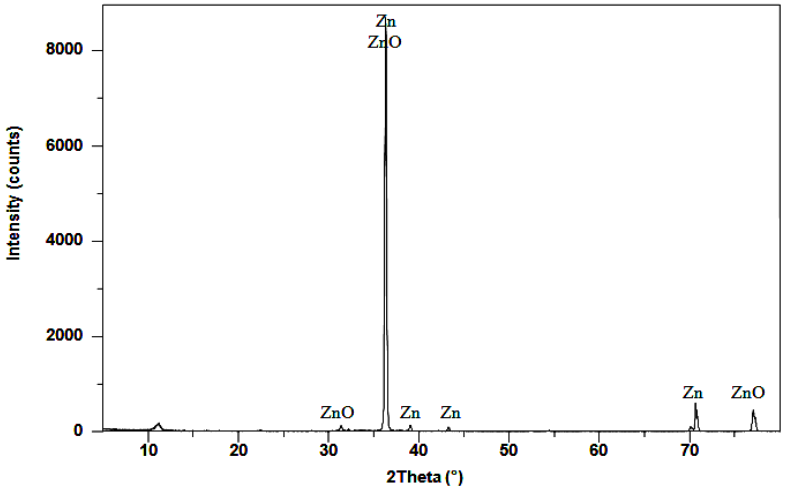

Fig: 2(a): XRD pattern of the new D-type battery anode

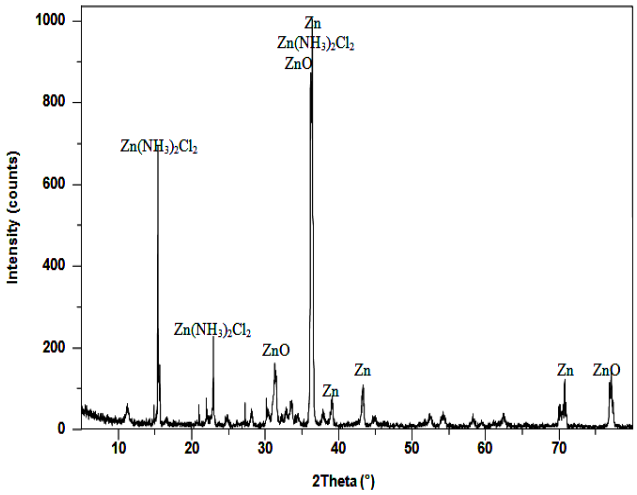

Fig: 2(b): XRD pattern of the spent D-type battery anode

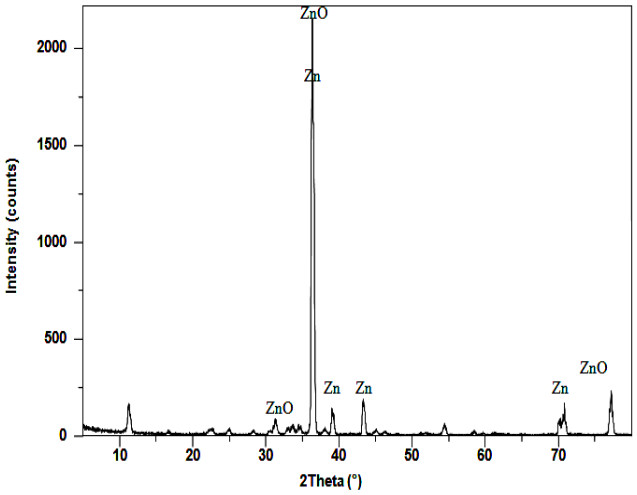

Fig: 2(c): XRD pattern of spent AA-type battery anode

A small amount of iron was detected in the spent anodes which come as a contaminant from the steel casing of the battery. A small amount of lead was also detected. However, no cadmium or mercury was detected in the anode. These elements were added in the past to improve the corrosion resistance of the anode as well as to improve the formability of anode zinc [6, 9]. Environmental regulations have obliged the battery manufacturers to exclude mercury and cadmium.

X-ray diffraction (XRD) patterns of the anodes of different type batteries are shown in Fig. 2. X-ray diffraction pattern of a new D-type anode [Fig. 2(a)] showed only Zn and ZnO as the

major phases on it. The most intense diffraction line of zinc and zinc oxide was found to be at almost the same angle and it was difficult to distinguish them. However metallic zinc should be expected to be predominant in new battery anodes. The results of chemical analysis, as presented previously, are in good agreement with this observation.

The most intense peak for zinc occurred at 36.2606^0 and for zinc oxide at 36.4345^0. The spent anode of a D-type battery [Fig. 2(b)] showed Zn, ZnO and $Zn(NH_3)_2Cl_2$ as the major phases. The presence of $Zn(NH_3)_2Cl_2$ could not be detected in the x-ray diffraction patterns of spent AA type battery anode [Fig. 2(c)]. The presence of $Zn(NH_3)_2Cl_2$ phase in the D-type battery electrolyte paste might be due to the presence of ammonium chloride in the electrolyte paste of the D-type batteries.

Table 5: XRF analysis of the electrolyte paste in different types of dry cell batteries*

No	Elements	AAA (wt %)		AA (wt %)		C (wt %)		D (wt %)		9V (wt %)		All types mixed
		New	Spent	New	Spent	New	Spent	New	Spent	New	Spent	
1	**Mg**	0.0730	0.168	0.0242	0.0762	0.163	0.0618	0.139	0.0663	0.103	0.0760	0.0648
2	**Al**	0.0876	3.31	0.0303	0.137	0.417	1.28	2.14	2.11	0.284	0.115	0.25
3	**Si**	0.261	5.77	0.161	0.108	1.79	2.17	1.95	1.35	0.566	0.293	0.15
4	**P**	0.007	0.198	0.0122	0.0103	0.0358	0.0687	0.0835	0.0667	0.0276	0.0137	0.0638
5	**S**	0.327	0.163	0.230	0.283	0.230	0.0409	0.0254	0.0230	0.281	0.284	0.157
6	**Cl**	**20.5**	**19.4**	**19.5**	**13.1**	**22.9**	**16.3**	**26.6**	**22.0**	**19.1**	**21.0**	**14.44**
7	**K**	0.0869	0.723	0.108	0.149	0.338	0.596	0.900	0.786	0.120	0.0844	0.481
8	**Ca**	0.208	0.654	0.132	0.232	0.529	0.197	0.730	0.495	0.452	0.170	0.569
9	**Ti**	-	0.101	-	-	-	0.0400	0.0658	0.0684	-	-	0.0383
10	**V**	-	0.0226	-	-	-	-	-	-	-	-	-
11	**Cr**	0.0386	0.0369	1.23	0.0368	-	0.0765	-	-	0.0237	0.0922	0.275
12	**Mn**	**65.3**	**47.9**	**58.2**	**60.9**	**56.9**	**41.6**	**54.6**	**60.2**	**58.2**	**64.2**	**60.1**
13	**Fe**	0.715	8.59	7.52	0.353	1.76	2.91	2.13	1.97	0.666	0.713	1.14
14	**Co**	-	0.0394	-	-	-	0.0444	0.0853	0.0918	-	-	0.0522
15	**Ni**	0.0175	0.137	0.0651	-	0.0134	0.0342	0.0718	0.0454	0.0159	0.0155	0.0626
16	**Cu**	-	0.0393	-	-	-	0.0249	0.0344	0.0454	-	-	0.0259
17	**Zn**	**12.4**	**12.7**	**12.7**	**24.7**	**14.8**	**34.4**	**10.2**	**10.4**	**20.2**	**12.9**	**22.07**
18	**As**	-	0.0190	-	-	0.0091	-	-	-	-	-	-
19	**Sr**	-	0.0580	-	-	0.0112	0.0206	0.0228	0.0148	-	-	0.0179
20	**Y**	-	0.0070	-	-	-	-	-	-	-	-	-
21	**Zr**	-	0.0045	-	-	-	-	0.0032	0.0024	-	-	0.0025
22	**Ba**	-	-	-	-	0.112	-	0.121	0.128	-	-	-
23	**Pb**	-	-	-	-	-	0.163	-	0.0335	0.0566	-	0.0400

* The analysis was done on dry basis and excluding the carbon, hydrogen and nitrogen content, as those elements can not be detected in XRF analysis

3.6. Characterization of the Electrolyte Paste

The percentages of various elements in the electrolyte paste of different types of zinc carbon batteries (both new and spent) are shown in Table 5. Zinc and manganese were the main metallic values in the electrolyte paste of both new and spent batteries. Chlorine was around 20 wt. percent and a very small percentage of lead was detected in some types.

The variation in composition may be ascribed to the difference in condition of the batteries when discarded and also to the variation in composition of electrolyte used by different manufacturers. The zinc and manganese contents of the spent batteries were seen to be more than in the new ones. This may be due to the dissociation of ammonium chloride in the spent batteries that consequently increased the metallic portions in these batteries. Higher zinc content in the electrolyte paste of the spent batteries could be due to the discharge reactions. A larger portion of the electrolyte paste than that of the anode was contaminated by iron.

Carbon and MnO_2 were found to be the major phases in the AAA, AA and C type new batteries [Fig.3(a)]. Carbon was found in several forms, i.e., graphite carbon, hexagonal carbon and cliftonite. Similarly, MnO_2 was found in several crystalline forms, like akhtensite, pyrolusite, ramsdelite, manganese black and manganese oxide. At least seven different types of MnO_2, representing several crystalline forms are known to exist [10]. NH_4Cl phase was predominant and clearly identified in the 9V and D-type new batteries of sunlight brand [Fig. 3(b)]. However, NH_4Cl phase could not be detected in the other three types of batteries due to the predominance of $ZnCl_2$ in such cells [6, 11].

In the spent batteries, $ZnO.Mn_2O_3$, Mn_2O_3 and Mn_3O_4 were the major phases (Fig. 4). This is in good agreement with the results obtained by other investigators [9]. Other probable phases present in those batteries were $MnO(OH)$,NH_4Cl, Fe_2O_3 and FeOCl. Iron contamination in the spent batteries comes from the oxidized outer steel part. The inter mixing of the steel casing and the electrolyte paste after a prolonged discharge time might occurred through the damaged layer of the zinc anode. Also, during dismantling, some outer oxidized steel parts would have mixed with the electrolyte paste.

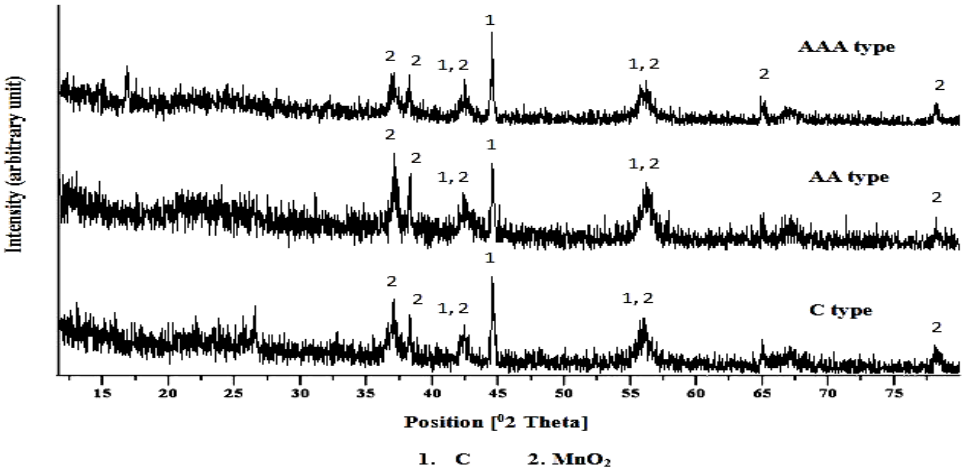

Fig. 3(a): XRD patterns of the AA, AA and C type new batteries

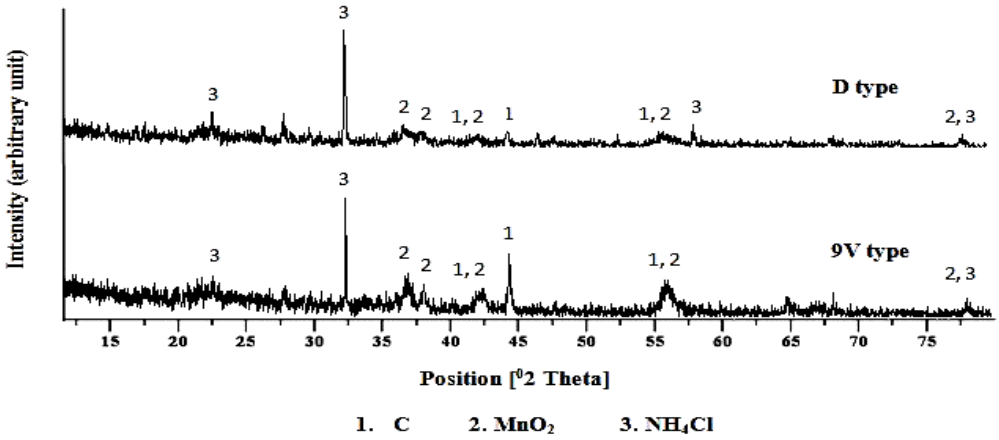

Fig. 3(b): XRD patterns of the D and 9V type new batteries

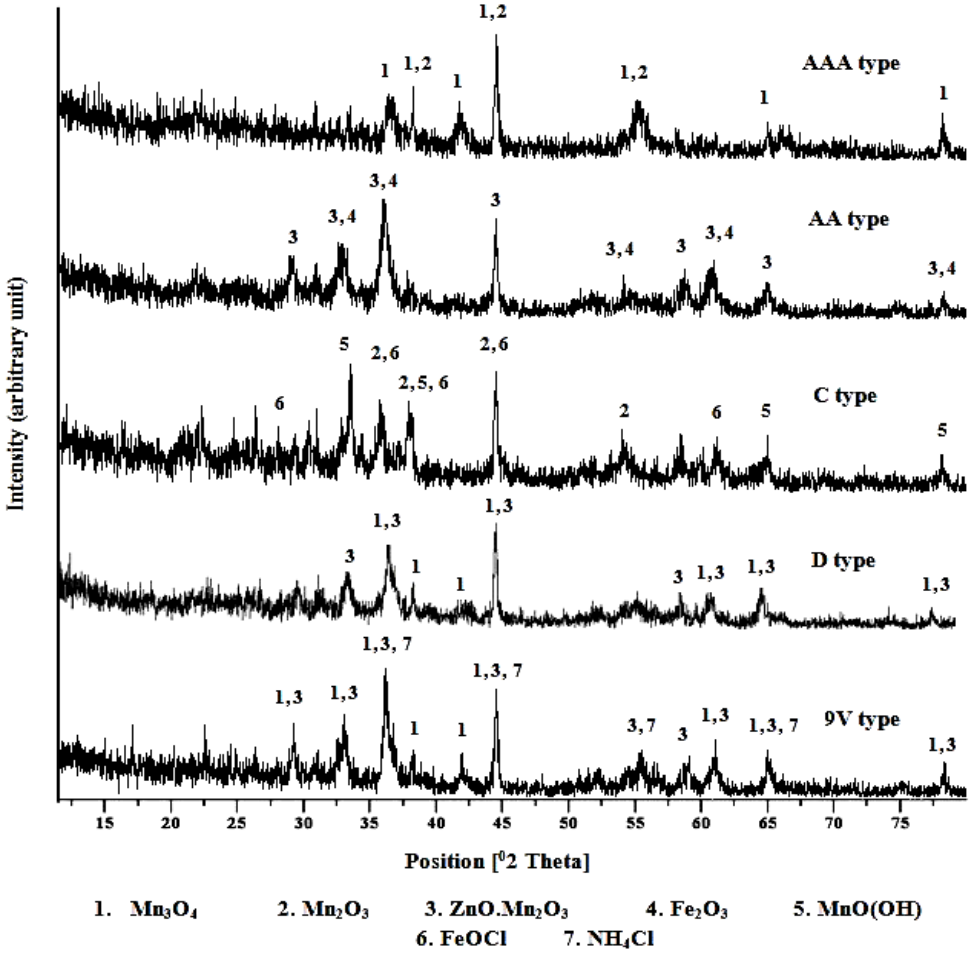

Fig. 4: XRD patterns of all the five type spent batteries

3.7. Total Metal Values

The average values of metal contents of the whole battery (both new and spent types) are given in Table 6 and Table 7 respectively. Small variations in the weight percentage of the elements were observed in the new and spent batteries. This may be attributed to the

variations in the amounts of non-metallic elements caused by probable ammonia dissociation in the spent types and also, to the variation in composition used by different manufacturers. Zinc and manganese contents were about 22 and 24 percent of the total weight of the battery in both the new and spent types. Steel parts constituted around 17 percent of the total weight. The carbon rod, chlorine, plastics, wax or asphalt and other minor elements constituted the remaining part of the batteries.

Table 6: Average metal wt. percentage in the new type Zn-C dry cell batteries *

	New batteries						Total value metals		
Types	**Total Weight (gm)**	**Zn casing (gm)**	**Paste (gm)**	**Amount of Zn (gm)**	**Amount of Mn (gm)**	**Amount of Steel Parts (gm)**	**% Steel parts**	**Total Zn %**	**Total Mn %**
AAA	7.20	2.48	3.28	0.337	1.776	0.202	**2.81**	**39.13**	**24.67**
AA	17.39	3.85	6.9507	0.732	3.353	3.5	**20.13**	**26.35**	**19.28**
C	48.68	8.37	26.07	3.199	12.298	8.43	**17.32**	**23.77**	**25.26**
D	90.036	15.015	49.30	3.711	19.864	13.22	**14.68**	**20.80**	**22.06**
9V	37.76	3.14	19.64	3.289	9.477	9.21	**24.39**	**17.03**	**25.10**
			Average				**17.19**	**21.94**	**23.26**

Table 7: Average metal wt. percentage in the spent Zn-C dry cell batteries*

	Spent batteries						Total value metals		
Types	**Total Weight (gm)**	**Zn casing (gm)**	**Paste (gm)**	**Amount of Zn (gm)**	**Amount of Mn (gm)**	**Amount of Steel Parts (gm)**	**% Steel parts**	**Total Zn %**	**Total Mn %**
AAA	7.2246	2.1266	3.44	0.363	1.368	0.1976	**2.74**	**34.46**	**18.94**
AA	17.7028	3.0056	7.607	1.558	3.841	3.5352	**19.97**	**25.78**	**21.70**
C	48.536	7.5405	26.538	7.57	9.153	8.4954	**17.50**	**31.13**	**18.86**
D	91.692	12.557	54.32	4.217	24.408	12.86	**14.03**	**18.29**	**26.62**
9V	36.53	2.578	20.297	2.167	10.782	8.394	**22.98**	**12.99**	**29.52**
			Average				**16.60**	**21.66**	**24.57**

* Total metal wt. % values have been determined on as received battery, thus including the moisture content of the paste.

4. CONCLUSIONS

The characterization of zinc-carbon batteries yielded the following results:

1. No mercury or cadmium was detected in the new and spent zinc-carbon type batteries.

2. Carbon was found to be around 4.5 wt. percent of the electrolyte paste in the spent battery.

3. Anode zinc was found over 99 percent pure with a very small percentage of lead in it.

4. ZnO was found to be the predominant phase in the anode of the spent battery.

5. In the electrolyte of the spent batteries, $ZnO.Mn_2O_3$, Mn_3O_4 and Mn_2O_3 were the main phases observed.

6. Zinc and manganese content were 46wt. percent of the total battery. Addition of steel parts to this analysis yielded a total metal values about 63wt. percent.

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