Journal of Metals, Materials and Minerals, Vol.21 No.2 pp.41-45, 2011

Recovery of Zinc from the Spent Zinc-Carbon Dry Cell Batteries Through Pyrometallurgical Route

Majharul HAQUE KHAN and A.S.W. KURNY

Materials and Metallurgical Engineering Department, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh

Abstract

Spent zinc-carbon batteries of all the five types (AAA, AA, C, D and 9V) were processed to recover zinc metal. All the components of the battery were separated, chemically analyzed and the anodic zinc parts were subjected to pyrometallurgical processing. Extraction of zinc was negligible when no fluxing agent was used. However, extent of recovery increased significantly when chloride salts: sodium chloride, calcium chloride and ammonium chloride were used as a fluxing agent. Among these, ammonium chloride gave the best result as flux. Using 10 %wt. of each flux, extraction of zinc was 90% for ammonium chloride, and around 75% for both sodium chloride and calcium chloride. A maximum 92% extraction of total zinc with purity over 99.5% could be obtained in presence of 12%wt. ammonium chloride flux by heating at 600°C for 10 minutes.

Key words : Spent Zn-C battery, Pyrometallurgy, Waste management, Fluxing agents

Introduction

Zinc-carbon type dry cell batteries is the oldest and most used type batteries in the world. In theses batteries, anode material is zinc and the cathode is a mixture of manganese dioxide and carbon. A very large quantity of these batteries is used in our daily lives and the batteries have a limited life. The disposal of the spent batteries, along with other municipal waste, in the landfill not only causes environmental hazards but also lead to the loss of these valuable metallic elements.

Depletion of the primary source of metals (ores) has compelled the current day researchers to search for alternatives. As a consequence of their efforts, zinc is now being extracted from several secondary sources; i.e. from galvanizing plant dross and ash, zinc scrap, flue dust generated from iron making and steel making plants, leach residues, spent primary batteries etc.(1, 2) Spent zinc carbon type batteries are very useful secondary resources to recover zinc as it constitutes almost 22 percent of the total weight of these type batteries. However, the zinc anode alone constitutes the maximum portion of zinc in these batteries.

Researchers have tried both hydrometallurgical and pyrometallurgical processes for recovery of zinc from the spent dry cell batteries. Hydrometallurgical process generally includes, dissolving the anode zinc in sulfuric or hydrochloric acid media, sometimes with prior water washing treatment and recovering the zinc from solution.(3, 4) Not many references to pyrometallurgical treatment of the anode zinc could be found in published literature. In one process, zinc containing portions were burned at a high temperature to make ash rich in zinc values and to remove the non metallic elements. Later, the zinc rich ash was leached in a suitable acid.(5) Pyrometallurgical processing of secondary sources of zinc other than spent primary batteries also has primarily focused on heating the components at a high temperature value and then reducing the oxides with a reducing agent like carbon.(6) Melting in presence of a suitable fluxing agent of the zinc rich secondary sources have been tried by some researchers.(7, 8)

The aim of the present study was to investigate the potential of recovering zinc from anodic parts of the zinc-carbon type dry cell batteries through pyrometallurgical route. Effect of

Email : aswkurny@mme.buet.ac.bd Tel: 8802 966 5618 Fax: 8802 861 3046

zinc was investigated and purity of the resulting zinc was also determined.

Materials and Experimental Procedures

Spent zinc carbon batteries were collected from different sources and a wide variety of zinc-carbon type dry cell battery could be found. All the five types (AAA, AA, C, D, 9V) of zinc-carbon dry cell batteries were collected. The whole battery was dismantled manually and weight distributions of different component parts were estimated. The anodic portion which was separated manually from different types batteries, were divided in batches weighing 20gm each. The anode zinc, having mixed with low amount of electrolyte paste and cardboard papers were heated in small crucible heater at around 600°C for about 10 minutes time, which was found to be the optimum temperature to melt and recover zinc from the anode.(7) A stirrer rod, made of stainless steel was used as a manual stirrer during melting of the anode zinc at that temperature. The molten zinc was poured in a metallic mould at around 550°C and subsequently was subjected to analysis for determining the purity of the product.

The anode zinc was characterized in Rigaku X-ray Fluorescence (XRF) machine to identify the composition. The operating voltage and current was 50 KV and 40mA. Also, the resulting ingot zinc was characterized in Shimadzu Optical Emission Spectroscopy (OES) machine with maintaining argon gas flow around 10 l/min during the experiment.

Results and Discussions

The anodic part in zinc-carbon type dry cell batteries is predominantly zinc, with purity over 99 percent.(10) Therefore extracting zinc from anodic parts alone should be noteworthy from the economic point of view. At first, melting of the anode zinc was tried without any fluxing agent additions. Later, the presence of chloride salts, such as ammonium chloride, sodium chloride, potassium chloride etc. were found to be effective for quick and lower temperature melting of the anode zinc of zinc-carbon dry cell batteries.(7, 9)

Weight Distribution of Different Component Parts

Average weight distributions in different component parts of all the five types of new and spent batteries were calculated and are shown in Table 1. The average was determined from computation of ten batteries each time.

Table 1. Comparison of different components parts of five type new and spent batteries.

Components	AAA type		AA type		C type		D type		9V type	
	New (gm)	Spent (gm)	New (gm)	Spent (gm)	New (gm)	Spent (gm)	New (gm)	Spent (gm)	New (gm)	Spent (gm)
Whole battery	7.20	7.2246	17.39	17.7028	48.68	48.536	90.036	91.692	37.76	36.53
Steel casing	-	-	3.10	3.093	6.80	6.7964	10.561	10.163	6.34	6.082
Polyethylene	0.10	0.1072	0.21	0.1908	0.44	0.4284	0.428	0.634	0.49	0.474
Zinc casing	**2.48**	**2.1266**	**3.85**	**3.0056**	**8.37**	**7.5405**	**15.015**	**12.557**	**3.14**	**2.355**
Upper steel plate (1)	0.092	0.0841	0.22	0.2238	0.91	0.935	1.258	1.315	2.87	2.376
Upper steel plate (2)	-	-	-	-	-	-	0.224	0.312	-	-
Lower steel plate	0.11	0.1115	0.18	0.2184	0.72	0.764	1.179	1.070	-	-
Cardboard paper	0.40	0.339	1.709	1.71	1.60	1.2969	5.51	5.51	4.71	4.572
Sealing rings					0.89	0.78	0.10	0.077	-	-
Electrolyte paste	**3.28**	**3.44**	**6.9507**	**7.607**	**26.07**	**26.538**	**49.30**	**54.32**	**19.64**	**20.297**
Carbon electrode	**0.55**	**0.5392**	**1.06**	**1.0836**	**2.70**	**2.6728**	**5.142**	**5.081**	**-**	**-**
Loss	0.247	0.474	0.11	0.57	0.18	0.78	1.31	0.65	0.57	0.374

Primary weight differences between the new and spent types were observed in anodic zinc parts and in the electrolyte paste. In all the five type of batteries, zinc is lower in amount in spent types than in the new ones. Again, weight of the electrolyte paste was found more in the spent types. This is due to the gradual corrosion of the anodic parts and later mixing the zinc portions in the electrolyte paste and hence, increasing its weight. Weight differences in any other parts were very negligible.

Pyrometallurgical Recovery of Zinc

Without Any Flux Addition

Zinc recovery from anodic parts of the dry cell batteries were first tried by simple melting without any flux addition and by heating at around 600^{0}C under manual stirring. Only a small coagulation of the zinc portions were observed in a random manner and no significant extraction of zinc could be achieved. Reason behind this could be attributed to the formation of oxide layer in the zinc parts (melting point of zinc oxide is 1975°C) and thus obstructing the coagulation. Resulting product was thus filled with slag where only some small fragments of zinc could be extracted.

Effect of Fluxing Agents

Different chloride salts as a fluxing agent were then examined to recover zinc from the anodic parts of the spent batteries. 10%wt. of sodium chloride, calcium chloride and ammonium chloride were used first. Use of fluxing agent increased the extent of recovery of zinc and, melting of zinc was clearly observed with slag portions being in the upper layer. Only a small amount of slag portions were identified with the fluxing agent additions.

Among the three chloride salts, ammonium chloride as a fluxing agent proved to be the best in terms of extent of recovery of zinc. Use of 10 %wt. ammonium chloride as a flux yielded around 90 % recovery of the anode zinc. Sodium chloride and calcium chloride gave verisimilitude result in percentage yield around 75%. The results of using different fluxing agents on the recovery efficiency of zinc are shown in Figure 1.

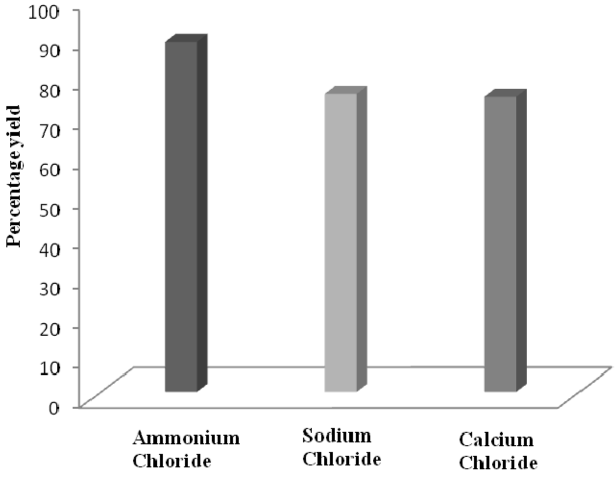

Figure 1. Fluxing agents' variation on the recovery percentage of anode zinc by pyrometallurgical treatment.

Results obtained with calcium or sodium chloride achieved a lower recovery percentage, probably due to the relatively high melting points of these two salts (>800°C)$^{(7)}$. The recovered zinc was over 99.5% pure with only a small percentage of lead on it as a major impurity. The OES analysis results of the product zinc obtained from these chloride fluxes are shown in Table 2.

Table 2. OES analysis of the product zinc for different fluxing agents

No.	Elements	%Wt.		
		Flux NH_4Cl	**Flux NaCl**	**Flux $CaCl_2$**
1	Mn	0.00021	0.00067	0.00064
2	Fe	0.02446	0.81998	0.02053
3	Cu	-	-	-
4	Ni	-	0.01292	-
5	Sn	0.00456	0.00393	0.00428
6	Al	-	-	-
7	Pb	0.38914	0.40619	0.31607
8	Mg	-	-	-
9	Cd	0.01733	0.01482	0.01438
10	Zn	99.564	98.741	99.644

Variation of NH_4Cl Flux in Zinc Recovery Efficiency

Percentage yield with the variation in amount of ammonium chloride flux is shown in Figure 2. Without any fluxing agents, recovery percentage of zinc was almost zero, as no coagulation of the mass product could be detected. Increasing the amount of ammonium chloride flux up to 12 %wt. increased the zinc recovery to a maximum of 92 %. Ammonium chloride, as a flux, dissociates at around 340°C and equal volume of ammonia and hydrogen chloride gas evaporates, creates a vapor blanket and restricts the atmospheric oxygen to react with the zinc. Also $Zn(NH_3)_2Cl_2$ phase formation occurs which helps to coalesce the zinc portions.(1, 7) With further increasing the flux portions decreased the extent of zinc recovery. This is due to the excess zinc ammonium chloride formation which attack more zinc and decrease the extent of recovery.(9) However, less than 12 %wt. flux could be sufficient for the similar recovery efficiency by making the crucible opening smaller and thereby reducing the atmospheric oxygen attack.

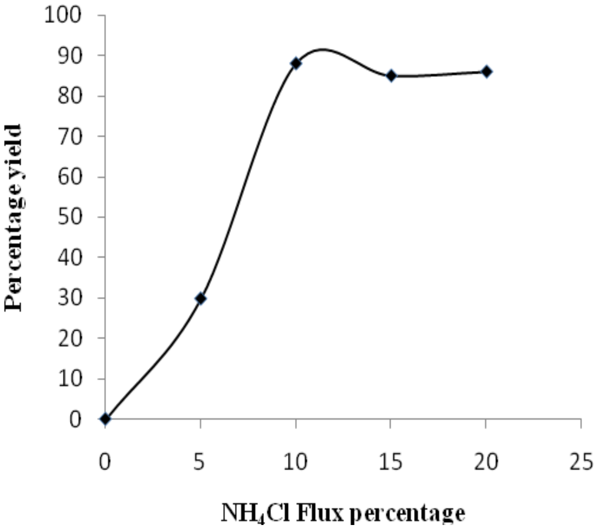

Figure 2. Ammonium chloride flux percentage variation for the maximum yield of zinc.

Recovery of zinc from the anode was also tried using the electrolyte paste of zinc-carbon type batteries, as the electrolyte paste itself contain some ammonium chloride. However, no zinc recovery was found when the electrolyte paste was used as a flux. This is due to the presence of very small amount of ammonium chloride in the electrolyte paste and also, for the dissociation of ammonia in atmospheric moisture present previously.

The slag portions that remained after the melting operation showed extensive amount of zinc in it on XRF analysis. It is to be emphasized that the quantity of slag that generated after each melting (with flux) was very small in quantity. Extent of slag was more when sodium chloride and calcium chloride were used as fluxing agents than when ammonium chloride was used as a flux. During melting, sufficient stirring was necessary to decrease the quantity of slag. Slag production was highest when no fluxing agents were used. The slag portions that accumulated from all the individual melting operations (with and without fluxing agent additions) were subjected to XRF analysis to identify the elements present. The result is shown in Table 3.

Table 3. XRF analysis of the slag obtained during zinc melting

No.	Component	%Wt. (Water washed sample)
1	MgO	0.140
2	Al_2O_3	1.27
3	SiO_2	1.31
4	P_2O_5	0.0385
5	SO_3	0.376
6	Cl	21.8
7	K_2O	0.180
8	CaO	3.15
9	Cr_2O_3	0.0398
10	MnO	7.61
11	Fe_2O_3	0.731
12	Co_2O_3	0.0294
13	NiO	0.0215
14	CuO	0.0207
15	ZnO	63.0
17	PbO	0.261

Zinc oxide was found over 63 %wt. in the slag and thus showed that a small quantity of zinc was lost in the slag portions. The remaining portions in the slag were mainly chlorine and manganese that came to slag portion from the electrolyte paste and fluxing agents' additions.

Conclusions

The pyrometallugical route to recover zinc from the anodic parts of spent zinc-carbon type dry cell batteries was examined. The study yielded the following results:

1. A certain amount of flux was essential for the recovery of zinc from the anodic portion of spent dry cell batteries.
2. As a fluxing agent ammonium chloride was better than sodium chloride or calcium chloride.
3. A maximum of 92% of anodic zinc could be recovered with 12 %wt. ammonium chloride flux.
4. Purity of the produced zinc ingot using ammonium chloride as a flux was over 99.5 % with only a small amount of lead on it.

Acknowledgement

The authors are grateful to Bangladesh University of Engineering and Technology (BUET) for providing the facilities needed. Authors are also grateful to the Director, Institute of Mining, Mineralogy and Metallurgy (IMMM) for his cooperation and encouragement.

References

1. Rabah, M.A. and Sayed, A.S. El. (1995). *Recovery of zinc and some of its valuable salts from secondary resources and wastes.* **37** : 23-32.

2. Strobos, J.G. and Friend, J.F.C. (2004). *Zinc recovery from baghouse dust generated at ferrochrome foundries.* **74** : 165-171.

3. Sayilgan, E., Kukrer, T., Yigit, N.O., Civelekoglu, G. and Kitis, M. (2010). Acidic leaching and precipitation of zinc and manganese from spent battery powders using various reductants. *J. Hazard. Mater.* **173**:137-143.

4. Michelis, I., Ferella, F., Karakaya, E., Beolchini, F. and Vegilo, F. (2007). Recovery of zinc and manganese from alkaline and zinc-carbon spent batteries. *J. Power. Sources.* **172** : 975-983.

5. Baba, A. A., Adekola, A. F. and Bale, R. B. (2009). Development of a combined pyro - and hydro - metallurgical route to treat spent zinc - carbon batteries. *J. Hazard. Mater.* **171** : 838-844

6. Bernades, A. M., Espinosa, D. C. R. and Tenorio, J.A.S. (2004). Recycling batteries: a review of processes and technologies. *J. Power Sources.* **130** : 291-298.

7. Rabah, M. A., Barakat, M. A. and Mahrous, Y.Sh. (1999). Recovering metal values hydrometallurgically from spent dry battery cells. *JOM.* **51(12)**

8. Bright, M.A., Deem, N.J. and Fryatt, J. (2007). The advantage of recycling metallic zinc from the processing wastes of industrial molten zinc applications., TMS.

9. Barakat, M.A. (2003). The pyrometallurgical processing of galvanizing zinc ash and flue dust., research summary. *JOM.*

10. Souza, C. C. B. M., Oliveira, D. C. and Tenorio, J. A. S. (2001) . Characterization of used alkaline batteries powder and analysis of zinc recovery by acid leaching. *J. Power. Sources.* **103** : 120-126.