

## Material Recycling of Used Primary Batteries

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**Abstract.** We developed equipment for the separation of a mixture of zinc-carbon and alkaline manganese batteries of the same size but different mass with the ultimate aim of recycling the valuable metals from these batteries. Using our equipment, we were able to separate these batteries with an accuracy of greater than 90%. After being dismantled, the metal content of each part of the battery was analyzed. For the alkaline manganese battery, post-treatment by potassium removal from the manganese cathode was necessary for material recycle. Potassium removal by hot water leaching was ineffective, but removal was possible using dilute hydrochloric acid leaching. The cathode of the zinc-carbon battery consisted mainly of manganese with low zinc and no potassium being present. Zinc contamination increased with battery discharge as it dissolved in the electrolyte.

**Keywords:** Material recycle, Separation, Alkaline manganese battery, Zinc-carbon battery

### 1. Introduction

Attempts are being made to recover used primary batteries to reduce the spread of mercury. Technical innovations have led to the wide distribution of non-hazardous mercury-free batteries which are generally disposed of in landfills [1, 2]. Since rechargeable batteries contain the rare metal lithium, technical developments for their recycling are being furthered [3, 4]. However, primary batteries contain mostly manganese and zinc with limited economic benefit and suitable recycling methods have therefore not been established.

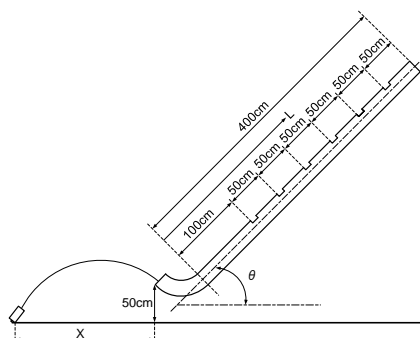


Fig. 1: Schematic diagram of battery separator designed in this work.

Although manganese is inexpensive, its import price varies according to the political and economical situation and it is therefore designated a rare metal in Japan. The establishment of recycling technologies for batteries containing manganese would be advantageous, assuming raw material prices remain stable for their manufacture.

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Manganese is required in the form of manganese dioxide in the battery manufacturing process. The reasonable chemical process is that manganese in spent batteries is converted to manganese sulfate, and reconverted to manganese dioxide after purification [5–7]. Researchers have investigated and suggested leaching, oxidation-reduction and precipitation techniques for spent batteries without prior separation of alkaline and zinc-carbon batteries [8, 9]. If impurities in the battery can be removed with reasonable cost, recycling may be a suitable alternative to using manganese ore. The removal of potassium is necessary as it prevents the manufacture of manganese dioxide of a suitable quality. Potassium is not used in zinc-carbon batteries but exists in large amounts in alkaline manganese batteries. Most of the zinc in zinc-carbon batteries exists in the metal casing, making separation recovery comparatively easily. However, in the alkaline manganese battery, zinc exists as a particulate paste making its separation from manganese powder difficult.

To address these recycling challenges, we separated used batteries into zinc-carbon and alkaline manganese batteries before dismantling them. Based on the experimental results obtained, a separation process is proposed.

## 2. Experiments and Results

### 2.1. Separation of zinc-carbon and alkaline manganese batteries

In previous reports [10], where we attempted metal recovery by dismantling used batteries, we noticed that the pre-separation of zinc-carbon and alkaline manganese batteries is important. In this work, a separator shown in Fig. 1 was designed and its operation assessed. The inner inclined vinyl chloride pipe was slid downwards to establish a suitable “jumping distance” for separation of the batteries.

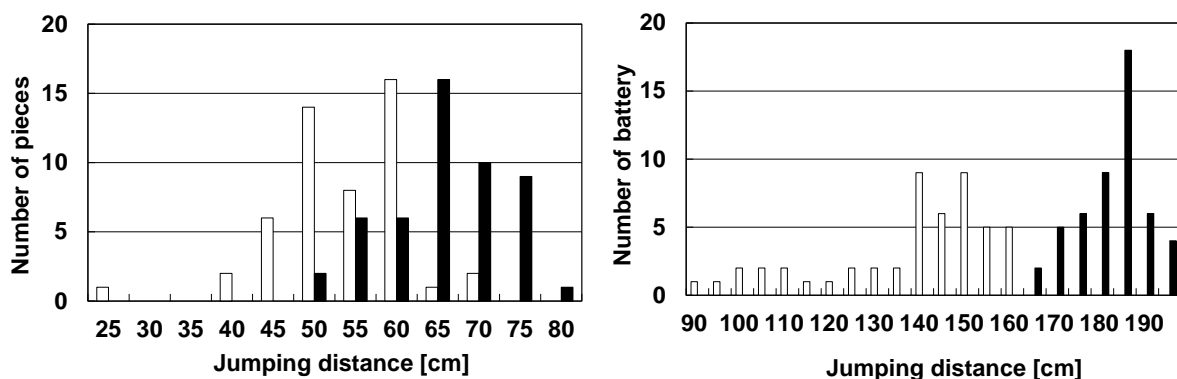


Fig. 2: Jumping distance distribution of size D batteries using battery separator. (a)  $L = 2$  m,  $\theta = 30^\circ$ ; (b)  $L = 2$  m,  $\theta = 45^\circ$ .  $\square$ , Alkaline manganese battery LR20;  $\blacksquare$ , Zinc-carbon battery R20.

An example of the jumping distance distribution for 50 size D batteries is shown in Fig. 2. For  $L = 2$  m and  $\theta = 30^\circ$ , the jumping distance distributions of the alkaline manganese LR20 and zinc-carbon R20 batteries overlap and separation is not possible. However, for  $L = 2$  m and  $\theta = 45^\circ$  the jumping distance is limited to 165 cm and the batteries are classified correctly. This simple device is effective for processing large quantities of batteries in a short time.

Table 1: Probability of separation [%] of batteries under various conditions using our separator.

Size		$L = 1$		$1.5$		$2$		$2.5$		$3$		$3.5$		$4$	
		$\theta = 30$	$45$	$30$	$45$	$30$	$45$	$30$	$45$	$30$	$45$	$30$	$45$	$30$	$45$
D	alkaline manganese battery LR20	89	96	84	100	77	100	76	98	81	98	68	100	73	81
	zinc-carbon battery R20	80	89	84	96	92	100	86	98	77	94	74	98	71	87
C	alkaline manganese battery LR14	74	67	76	67	77	69	60	88	59	84	50	78	50	74
	zinc-carbon battery R14	83	64	76	61	74	80	58	88	61	82	50	78	50	77
AA	alkaline manganese battery LR6	91	72	85	78	93	68	89	58	98	61	96	61	100	65
	zinc-carbon battery R6	87	72	81	66	87	60	94	56	100	64	89	61	98	63

Table 1 shows the accuracy of separation of each battery for each size for various values of  $L$  and  $\theta$ . Size D and AA batteries could be separated with an accuracy of more than 98%. The highest separation for size C batteries was 88%. However, when the spent battery label is degraded or if the surface is rusty from storage conditions, the accuracy of separation decreases.

## 2.2. Dismantling of batteries

Two types of batteries were dismantled by radial cutting as discussed in our previous report [10] (see Fig. 3). For the zinc-carbon battery, the outer casing and zinc were sectioned approximately 3 mm from the positive terminal for removal of the inner manganese cathode and carbon rod. For the alkaline manganese cell battery, the outer casing was sectioned at 3 mm from both the positive and negative terminals for removal of the inner zinc anode and manganese cathode in the middle layer. The zinc and manganese are wet and form a paste with potassium hydroxide solution. All parts were washed with water and weighed after drying. To assess the effect of use, a new battery was discharged from initial 1.5 V to 1.2 or 0 V over several hours using a 10  $\Omega$  resistance.

Table 2: Elemental composition in manganese and zinc parts of alkaline manganese battery LR20.

Remaining voltage [V]	Manganese cathode part [wt%]				Zinc anode part [wt%]			
	Mn	Zn	K	Other	Mn	Zn	K	Other
1.5	55.3	0.7	9.1	34.9	0.2	89.2	2.6	8.1
1.2	54.6	1.0	8.8	35.6	0.1	81.4	2.5	16.0
0	53.0	1.0	9.0	37.0	0.3	72.4	2.1	25.2

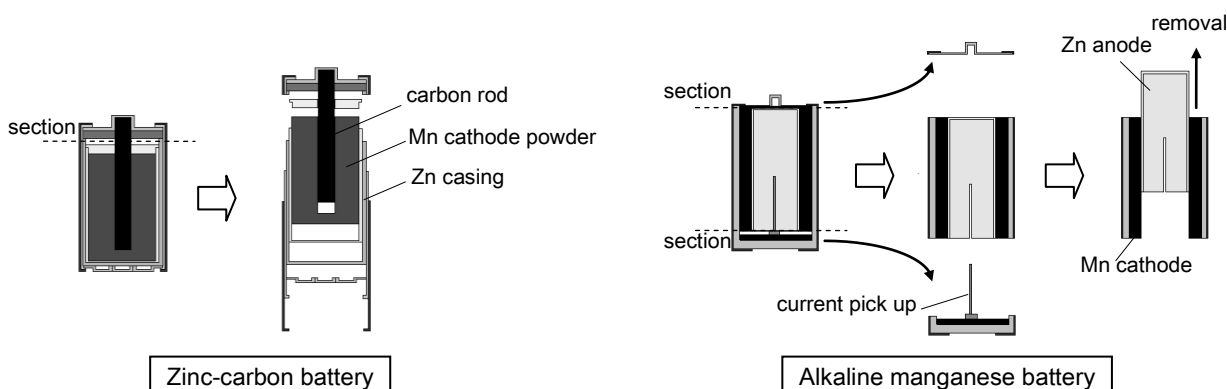
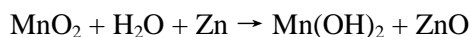


Fig. 3: Dismantling of dry cell batteries.

## 2.3. Recycling of alkaline manganese battery

The chemical reaction for the discharge of the alkaline manganese battery proceeds according to:



The valuable metal components of the alkaline manganese battery are zinc, manganese and brass. The inner zinc layer is a microparticulate paste in potassium hydroxide solution.

Table 2 gives the chemical analysis of the manganese and zinc in the alkaline manganese battery measured by atomic absorption spectrometry (Shimadzu, AA-7000F). The minimal contamination of zinc in the manganese cathode is not considered to be problematic. However, the potassium content is high and further purification would be required for recycling. The high zinc content in the anode can be recovered without chemical processing.

The manganese cathode was leached with hot water at 60  $^{\circ}\text{C}$  and with 1 and 5 % hydrochloric acid solutions to remove the potassium. After 20 min, the potassium content was determined. As shown in Table 3, leaching with hot water was insufficient and the potassium leached increased for the more highly

discharged batteries. Acid leaching was more effective but leaching at high acid concentration resulted in some manganese dissolution.

Table 3: Purification of manganese cathode of LR20 by leaching.

Leaching liquid	Remaining voltage	Elemental content [wt%]			
	[V]	Mn	Zn	K	Others
Hot water (60 °C)	1.5	53.7	0.2	1.8	44.3
	1.2	53.3	0.2	2.4	44.1
	0	53.0	1.1	3.7	42.2
1 % HCl (room temp.)	1.5	55.4	0.0	0.0	44.6
	1.2	53.7	0.0	0.1	46.2
	0	53.1	0.0	0.3	46.6
5 % HCl (room temp.)	1.5	53.4	0.0	0.0	46.6
	1.2	52.0	0.0	0.0	48.0
	0	51.1	0.0	0.2	48.7

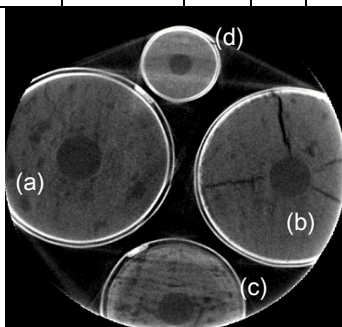


Fig. 4: Inner structure of zinc-carbon battery observed by X-ray CT.  
(a) New R20, (b) Used R20,  
(c) Used R14, (d) Used R6

## 2.4. Recycling of zinc-carbon battery

The valuable metal components in the zinc-carbon battery are zinc and manganese. The chemical reaction for the battery discharge is:

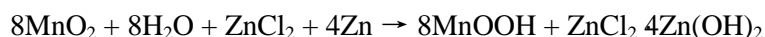


Fig. 4 shows the inner structure of the zinc-carbon battery observed by microfocus X-ray computed tomography (TESCO, HMX225-ACTIS+3). The shrunken and solidified manganese powder in the used battery will require increased handling and cost.

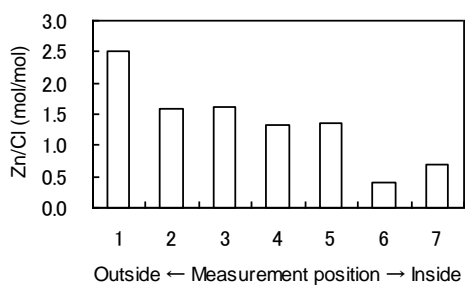


Fig. 5: Zinc content distribution inside zinc-carbon battery R20 discharged to 0 V.

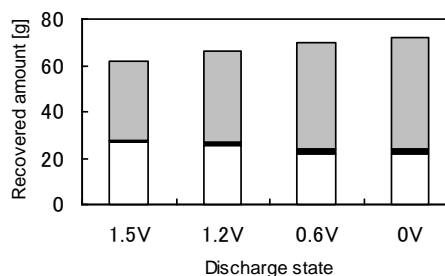


Fig. 6: Recovered mass and composition of manganese from zinc-carbon battery R20. □, Manganese; ■, Zinc; ▒, Others.

Zinc elution into the manganese powder part with discharge was measured by spot type X-ray fluorescence analyser (AMETEK, Orbis PC). Since the electrolysis solution is  $ZnCl_2$ , the molar ratio of zinc to chlorine is 0.5 under standard conditions. As shown in Fig. 5, for the 0 V discharge, the outer zinc content was higher than the standard value. The chemical content of the used battery therefore differs according to position. Fig. 6 shows the elemental analysis and recovered manganese. The amount of manganese increased with discharge caused by the oxidation reaction during battery use. Some contamination by zinc was also observed. Although not perfect, the recycle of materials from the zinc-carbon battery should be possible.

### 3. Conclusion

The automated separation of alkaline manganese and zinc-carbon batteries was possible with an accuracy of 90% or more. The probability for separation decreased with surface deterioration of the waste battery and it was therefore necessary to devise a means to improve this accuracy.

The manganese and zinc parts of the battery could be separated by dismantling the battery. For the alkaline manganese battery, the manganese cathode was contaminated with potassium. By dilute hydrochloric acid leaching, it was possible to remove the potassium. Also, it was possible to obtain good quality zinc without post-treatment. For the zinc-carbon battery, it was possible to prevent contamination of potassium by pre-separation with alkaline manganese battery. However, corrosion during battery use makes zinc recovery difficult. Moreover, manganese solidification during battery discharge made dismantling of the battery difficult.

### 4. Acknowledgements

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