TRANSLATION:

1994 STUDY REPORT ON AN INVESTIGATION OF THE EFFECT OF BURYING USED ALKALINE DRY BATTERIES IN THE SOIL

CONTRACT RESEARCH GROUP: WATER SCIENCE AND SANITARY ENGINEERING LABORATORY, DEPARTMENT OF CIVIL ENGINEERING, FACULTY OF ENGINEERING, FUKUOKA UNIVERSITY

March 1995

Japan Battery and Appliance Industries Association (Corporation)

Urban city cleaning vol 49. No.212 (June 1996) P.47

Behavior of Mercury in used dry batteries buried in landfill sites

Behavior of Mercury in used dry batteries buried in landfill sites

Urban city cleaning vol 49. No.212 (June 1996) P.47

Ryuji Yanase
Shigeru Oho
Yasushi Matsufuji
Masataka Hanashima

Fukuoka University

1 Introduction

The mercury in discarded used dry batteries was suspected of leading to environmental pollution and was brought into question as a possible environmental problem around 1983 in Japan. At the end of 1990, zinc–carbon battery with no added mercury was achieved and at the end of 1991, alkaline manganese battery with no added mercury was achieved successively in Japan and thus the mercury in used dry batteries is not a issue of social concern any more. However, behavior of mercury in used dry batteries buried in landfill sites has not yet been sufficiently studied.

We have started burying experiments of used dry batteries from 1985 to investigate mainly the following items.

a) Leaching rate of mercury and other heavy metals.
b) Vaporization rate of mercury.
c) Corrosion of used dry batteries in small scale burying tanks.

In September 1995, ten(10) years have passed after the burying experiments have started and we have dismantled four(4) anaerobic tanks out of eight(8) large–scale experimental burying tanks. We report the followings in this paper.

a) Leaching rate of mercury from anaerobic burying tanks in the past ten(10) years.
b) Corrosion of used dry batteries in anaerobic burying tanks in the past ten(10) years.
c) Corrosion of used dry batteries in small–scale experimental burying tanks.

2 Experimental burying tanks and conditions

Table 1 shows experimental conditions in total of eight(8) large-scale experimental burying tanks of both semi-aerobic type and anaerobic type. In this paper, experimental results in anaerobic burying tanks (Fig. 1) are summarized and reported. As shown in Table 1, we had the following four(4) anaerobic burying tanks.

Tank No. V : mixture (mercury, alkaline manganese, zinc-carbon)
Tank No. VI : alkaline manganese
Tank No. VII : zinc-carbon
Tank No. VIII : blank

A specified number of dry batteries as shown in Table 1 was packed every 10cm of the height of garbage in the tank as that dry batteries are uniformly distributed in garbages. The amount of garbage packed per tank was four(4) tons. Composition of packed garbage is shown in Table 2. As can be seen from Table 2, packed garbage consisted of non-combustibles. As shown in Table 3, mercury battery, alkaline manganese battery and zinc-carbon battery were packed in the tank. The number of packed batteries was adjusted so that total mercury amount becomes close to the mercury content at the burying landfill sites.

Mercury content in the packed garbage and dry batteries is shown in Table 2 and Table 3, respectively. Total amount of mercury in each tank is shown in Table 4. Natural rainfall was selected as rainfall condition and surface runoff water was drained.

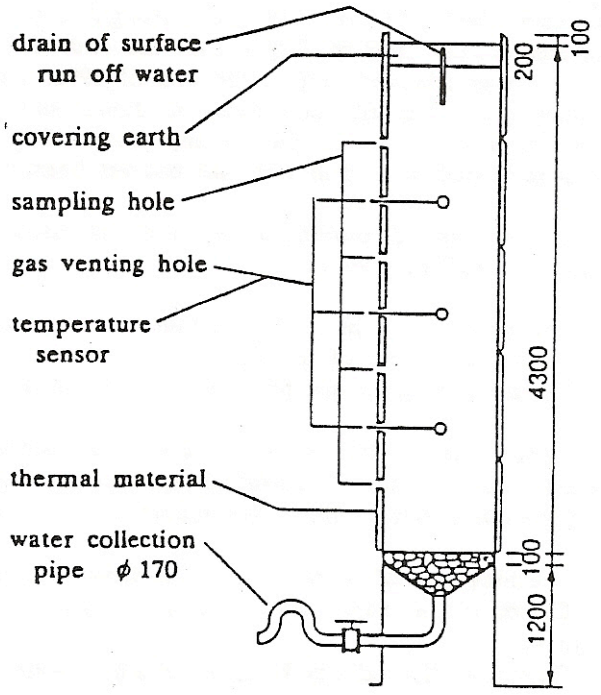


Fig. 1 Anaerobic burying tank

Table 1 – Amount of garbage and number of dry batteries packed in the tank

burying condition		semi–aerobic				anaerobic			
tank		I mixture	II alkaline manganese	III zinc–carbon	IV blank	V mixture	VI alkaline manganese	VII zinc–carbon	VIII blank
weight of garbage (ton)		4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
weight of garbage per unit volume (t/m^3)		1.18	1.18	1.18	1.18	1.18	1.18	1.18	1.18
weight of covering earth (kg)		218	220	220	220	220	220	221	220
weight of covering earth per unit volume (t/m^3)		1.38	1.40	1.40	1.40	1.40	1.40	1.41	1.40
number of dry batteries (pieces)	MR9	4	0	0	0	4	0	0	0
	LR6	32	80	0	0	32	80	0	0
	R20	80	0	80	0	80	0	80	0
	R14	80	0	80	0	80	0	80	0
	R6	240	0	240	0	240	0	240	0
	total	436	80	400	0	436	80	400	0

Table 2 – Composition of packed garbage and mercury content

packed garbage	composition (%)	mercury content (mg/tank)
incinerated ash	38	227
trees and plants (chips)	5	0.4
plastics	2	0
glass (crushed)	20	3.2
metal (empty cans)	4	40
metal (steel sheets)	6	0
sewage sludge	15	343
sludge (compost)	10	172
sandy soil	–	2.9
total	100	789
mercury / ton of packed garbage	–	197

Table 3 – Number of dry batteries packed in the tanks and mercury content

dry battery	mercury content (mg/piece)	mixture tank		alkaline manganese tank		zinc–carbon tank	
		pieces	mg	pieces	mg	pieces	mg
MR9	1,260	4	5,040	–	–	–	–
LR6 (1)	190	–	–	28	5,320	–	–
LR6 (2)	124.8	32	3,994	52	6,490	–	–
R20	4.37	80	350	–	–	80	350
R14	2.17	80	174	–	–	80	174
R6	1.50	240	360	–	–	240	360
total	–	436	9,918	80	11,810	400	884
per ton	–	109	2,480	20	2,953	100	221

LR6 (1) : production of Dec. 1984, LR6 (2) : production of Feb. 1985

Table 4 – Total amount of mercury in each tank

tank	mixture	alkaline manganese	zinc–carbon	blank
packed garbage (mg/tank)	789	789	789	789
dry battery (mg/tank)	9,918	11,810	884	0
total (mg/tank)	10,707	12,599	1,673	789
per ton (mg/ton)	2,677	3,150	418	197

tank	mixture	alkaline manganese	zinc–carbon	blank
packed garbage (mg/tank)	789	789	789	789
dry battery (mg/tank)	9,918	11,810	884	0
total (mg/tank)	10,707	12,599	1,673	789
per ton (mg/ton)	2,677	3,150	418	197

Table 3 – Number of dry batteries packed in the tanks and mercury content

dry battery	mercury content (mg/piece)	mixture tank		alkaline manganese tank		zinc–carbon tank	
		pieces	mg	pieces	mg	pieces	mg
MR9	1,260	4	5,040	–	–	–	–
LR6 (1)	190	–	–	28	5,320	–	–
LR6 (2)	124.8	32	3,994	52	6,490	–	–
R20	4.37	80	350	–	–	80	350
R14	2.17	80	174	–	–	80	174
R6	1.50	240	360	–	–	240	360
total	–	436	9,918	80	11,810	400	884
per ton	–	109	2,480	20	2,953	100	221

LR6 (1) : production of Dec. 1984, LR6 (2) : production of Feb. 1985

Table 4 – Total amount of mercury in each tank

tank	mixture	alkaline manganese	zinc–carbon	blank
packed garbage (mg/tank)	789	789	789	789
dry battery (mg/tank)	9,918	11,810	884	0
total (mg/tank)	10,707	12,599	1,673	789
per ton (mg/ton)	2,677	3,150	418	197

tank	mixture	alkaline manganese	zinc–carbon	blank
packed garbage (mg/tank)	789	789	789	789
dry battery (mg/tank)	9,918	11,810	884	0
total (mg/tank)	10,707	12,599	1,673	789
per ton (mg/ton)	2,677	3,150	418	197

3 Results and discussion

3.1 Mercury balance in anaerobic burying tank

(1) Amount of mercury in the leachate;

We have measured the amount of mercury in the leachate which flows out of the burying tank every month Fig. 2 shows the annual average of Hg concentration over time. As can be from Fig. 2, annual average concentration of each tank was as low as 0.0001mg/ℓ – 0.00035mg/ℓ for ten(10) years. These values are found to be lower than environmental standard of 0.0005mg/ℓ.

It is considered possible that some amount of mercury was vaporized from corroded dry batteries in the tank and dissolved in the leachate. However, we did not find any significant difference of the amount of mercury in the leachate between tanks No. V, VI, VII (with dry batteries) and tank No. VIII (without dry batteries). Consequently, we can reasonably assume that the dissolved amount of vaporized mercury from corroded dry batteries is negligibly small.

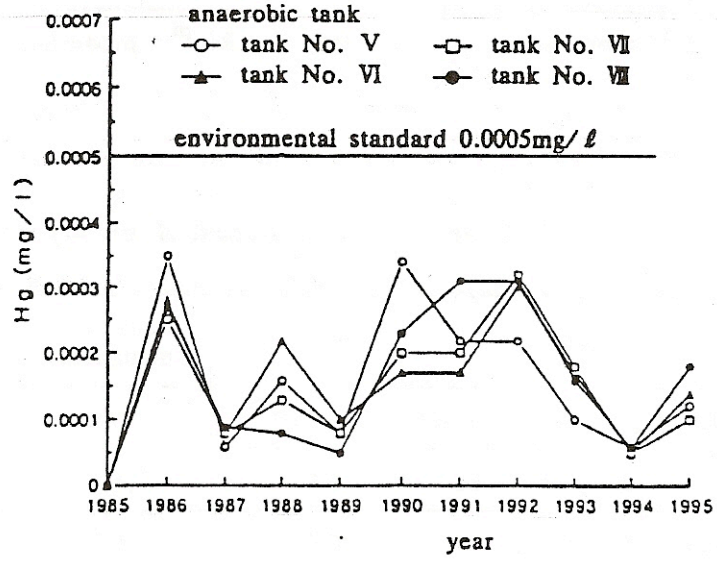


Fig. 2 Change of the Hg concentration in the leachate over time (annual average)

(2) Diffusion of vaporized mercury;

Since mercury vaporizes at room temperature, we have measured the concentration of vaporized mercury from landfill sites. Results are shown in Fig. 3. It was found that the concentration of vaporized mercury was 0.1 – 0.4 μ g/m³. This value is about 10 – 100 times higher than normal concentration of gaseous mercury in the atmosphere but about 1/10 – 1/100 times of the guideline defined by WHO. We did not find any significant difference of the amount of vaporized mercury between tanks No. V, VI, VII (with dry batteries) and tank No. VIII (without dry batteries), either. Consequently, we can also reasonably assume that the amount of vaporized mercury from corroded dry batteries is negligibly small.

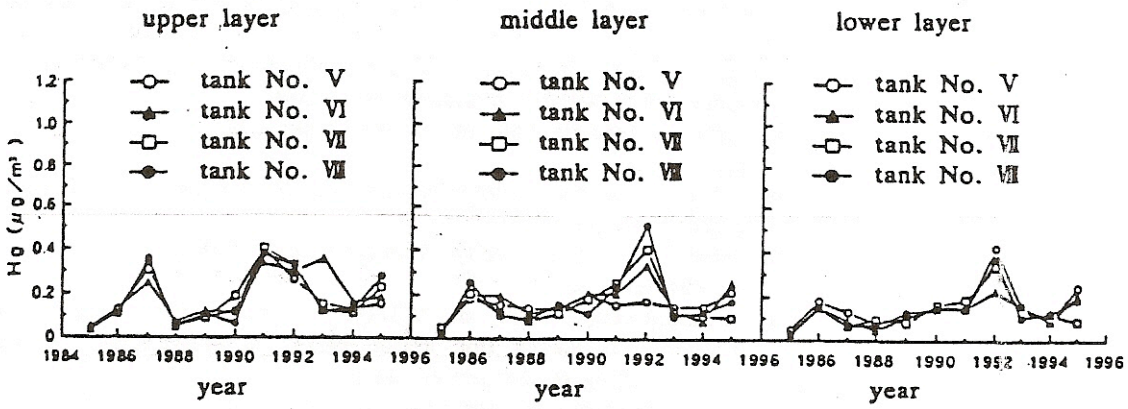


Fig. 3 Change of vaporized Hg over time in anaerobic tank (annual average)

(3) Mercury balance;

We have dismantled large-scale anaerobic tanks and are now studying the mercury balance in both dry batteries and garbages packed in these tanks. We explain the mercury balance in 9.5 years after the burial of tanks before dismantling them in the following.

We assumed as follows for the calculation of mercury balance.

① Amount of mercury in the leachate can be calculated by the following formula;
Mercury concentration per month (N.D = 0.0001mg/ℓ) × accumulated amount of leachate.

② Amount of vaporized mercury diffused in the air can be calculated by the following formula;
Annual average concentration of each layer (upper, middle, lower) × accumulated amount of gas generation from the buried tank.

Fig. 4 shows the results of our estimation. As to mercury balance in tank No. V (mixture tank), we can comment as follows.

a) Initial mercury content in the tank; 10.71g (9.29g in dry batteries and 0.79g in garbages).
b) Mercury amount which leached in the leachate in 9.5 years; 0.008% of the initial mercury content.
c) Mercury amount which vaporized and diffused in the air; 0.003% of the initial mercury content.
d) Consequently, total of 0.011% of the initial mercury content has leached or diffused. It means that about 99.9% of the mercury is reasonably estimated to be still remaining in the buried tank.
e) Total amount of mercury escaped from the four(4) tanks (V, VI, VII, VIII) by leaching or diffusion ranges 1.04 – 1.16mg and there is no significant difference among those values of four(4) tanks. Consequently, we did not find any significant difference of the amount of escaped mercury due to the difference of initial mercury content in the tank.

From these results, we can reasonably estimate that the mercury escaped from garbages or dry batteries in the tank were mostly absorbed in the garbages and were very difficult to flow out of the tank, and as a result, almost all amount of mercury are still remaining in the tank. Consequently we have found that mercury is escaping from buried tanks very slowly.

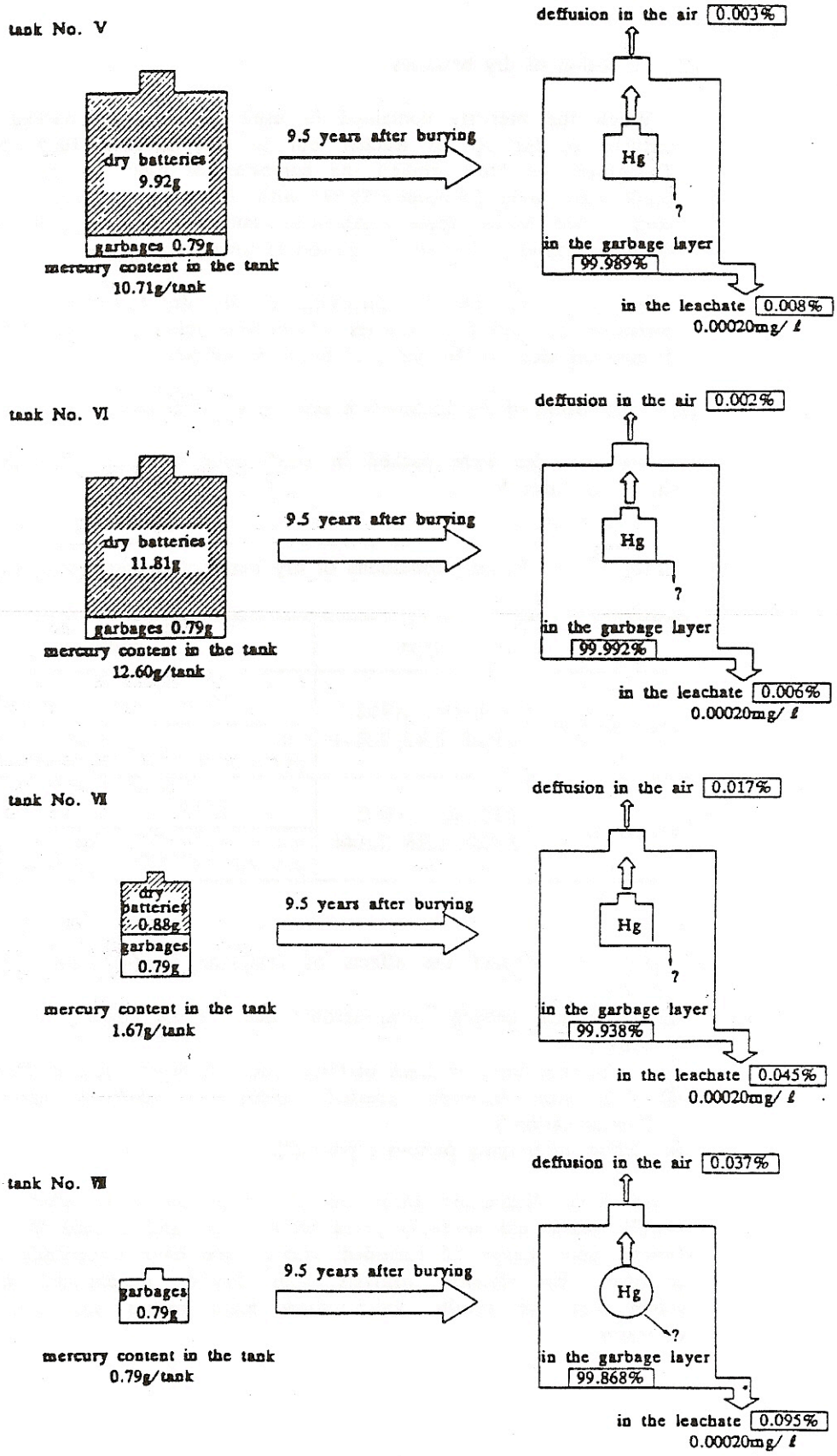


Fig. 4 Mercury balance in anaerobic burying tanks (after 9.5 years)

3.2 Corrosion of dry batteries

When the mercury contained in used dry batteries packed in tanks vaporizes and diffuses in the air or leaches out in the leachate, they should first be corroded. Therefore, we have studied the corrosion of used dry batteries by packing them in small–scale tanks (ϕ 30cm × 85cm) with the same garbages as we packed in large–scale tanks. We buried these small–scale tanks in the same landfill sites and dismantled them successively after certain period of time.

We have compared the corrosion of used dry batteries in small–scale tanks and the corrosion of used dry batteries which were taken out from anaerobic large–scale tanks dismantled after ten(10) years of burial as follows.

(1) Corrosion of dry batteries in small–scale experimental tanks;

Dry batteries were packed in small–scale experimental tanks on the conditions as shown in Table 5.

Table 5 – Packing conditions of dry batteries in small–scale experimental tanks

	type	condition				pieces
semi–aerobic	R20, R6, MR52 LR20, LR6, LR44	fresh		discharged		24 pieces/tank
		not pressed	pressed	not pressed	pressed	
anaerobic	R20, R6, MR52 LR20, LR6, LR44	fresh		discharged		24 pieces/tank
		not pressed	pressed	not pressed	pressed	

We have studied the effects of following four(4) items on the corrosion of dry batteries.

① Difference between semi–aerobic and aerobic burying tanks ("condition of burying tank").
② Difference between fresh batteries and discharged batteries ("battery voltage").
③ Difference between pressed (deformed) batteries and not–pressed batteries ("deformation").
④ Effect of burying periods ("period").

We have dismantled these buried small–scale tanks after half year, one(1) year, two(2) years and seven(7) years after burial and studied the weight change, voltage change and change of corroded areas. We have statistically analysed the causes of corrosion by variance analysis with four(4) dimensional arrangement. Table 6 summarizes the results which show main causes and their contributions to the corrosion.

Table 6 – Contribution of various factors to the corrosion area of dry batteries

battery / cause	R20			R6			LR20		
	1 year	2 years	7 years	1 year	2 years	7 years	1 year	2 years	7 years
(A) condition of burying tank	***12.1	*** 9.2	* 4.0	***26.5	***17.9	** 7.3	***15.6	***14.1	*** 6.6
(B) battery voltage	***40.5	***34.4	***36.8	***51.5	* 18.6	***19.7	***46.4	***47.9	***49.3
(C) deformation	–	–	–	–	* 2.5	–	** 5.6	–	–
(D) period	*** 6.8	** 9.5	***22.9	* 2.3	** 13.5	***24.4	** 5.9	* 3.6	*** 9.3
A × B	***18.0	***12.0	** 5.1	*** 8.6	–	–	* 5.6	–	–
A × C	–	* 2.4	–	* 1.6	–	(*) 5.3	–	–	–
A × D	*** 6.9	** 6.2	–	–	–	–	–	* 6.1	** 7.4
B × C	–	–	–	–	–	–	–	* 3.4	(*) 1.7
B × D	*** 7.8	** 6.2	* 7.2	* 2.1	***21.0	** 12.1	** 6.3	(*) 2.5	–
C × D	–	–	–	–	* 4.7	* 6.4	* 4.6	–	–
A × B × C	–	–	–	* 1.7	–	–	–	* 2.4	–
A × B × D	*** 5.1	** 6.2	(*) 2.7	–	* 4.8	–	–	** 8.4	*** 9.8
A × C × D	–	–	–	–	* 3.5	–	–	–	–
B × C × D	–	–	–	–	* 4.0	(*) 2.7	* 3.0	–	–

battery / cause	LR6			LR44			MR52		
	1 year	2 years	7 years	1 year	2 years	7 years	1 year	2 years	7 years
(A) condition of burying tank	–	–	(*) 0.1	(*) 4.3	–	–	***21.7	***15.2	(*) 2.5
(B) battery voltage	***80.8	***48.2	***41.4	***29.2	***32.3	***30.7	***37.0	***26.0	***24.2
(C) deformation	–	* 5.3	* 4.9	(*) 4.4	–	(*) 1.6	* 3.1	* 3.0	–
(D) period	(*) 2.4	–	(*) 7.6	–	–	* 7.8	–	–	(*) 5.1
A × B	–	–	–	***24.7	** 13.1	***18.2	***16.7	***13.6	(*) 2.1
A × C	–	–	–	* 9.8	(*) 3.9	–	** 6.3	** 4.4	(*) 2.0
A × D	–	–	–	–	–	–	–	** 5.0	(*) 5.1
B × C	–	–	(*) 0.4	* 7.7	–	–	* 3.8	** 6.3	–
B × D	(*) 2.8	***21.3	* 10.2	–	–	–	–	** 9.1	(*) 1.6
C × D	–	–	–	–	–	–	–	–	(*) 3.7
A × B × C	–	* 3.3	–	–	–	–	* 4.6	*** 6.8	–
A × B × D	–	–	(*) 4.1	–	* 6.3	(*) 4.9	–	* 2.7	(*) 3.0
A × C × D	* 2.9	–	–	–	(*) 4.3	–	–	(*) 1.6	–
B × C × D	–	–	–	–	* 11.9	* 7.2	–	. –	(*) 0.7

*** percentage of risk 0.5% ** percentage of risk 1.0% * percentage of risk 5.0%
(*) percentage of risk 10.0%

(A) "condition of burying tank" (B) "battery voltage" (D) "period", and (B) × (D) showed high contribution to the corrosion.

After seven(7) years, average contribution rates were as follows;

(A) : 5.8%
(B) : 33.3%
(D) : 18.3%
(B) × (D) : 9.7%

From the above results, we can find that (B) "battery voltage" has a high contribution to the corrosion.

Contribution of (A) "condition of burying tank" has decreased as burying period becomes longer. We assume the reason to be as follows. At the initial period, quality of leachate was different between semi-aerobic type and anaerobic type. However, they will become almost the same in a long period. At the initial period, these differences in the quality of leachate and decomposition rate of garbages seem to affect the contribution.

Regarding (B) "battery voltage", it has high contribution after one(1) year and there is no significant difference between that of after two(2) years and seven(7) years. As a result, batteries seem to be mainly corroded electrolytically and effect of battery voltage is not eminent after two(2) years. (D) "period" was found to have higher contribution as burying period becomes longer.

For these dry batteries, which showed difference of corrosion with 95% confidence limit, average corrosion area rate of main factors are shown in Fig. 5. From Fig. 5, it was found that anaerobic type and fresh battery have higher corrosion rates than semi-aerobic type and discharged battery, respectively. It was also found that corrosion proceeds rather quickly between half year and one(1) year after burial and it proceeds rather slowly after one(1) year of burial.

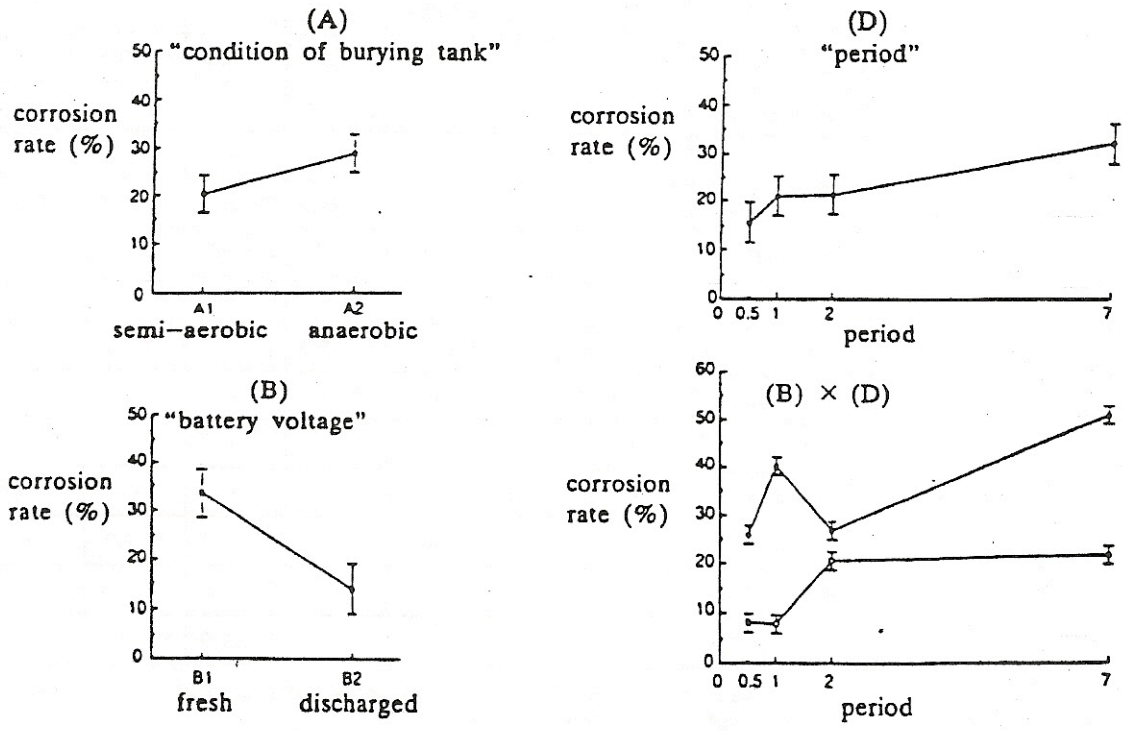


Fig. 5 Average corrosion area rate of main factors (95% confidence limit)

(2) Corrosion of used dry batteries after ten(10) years of burial;

We have dismantled anaerobic type large-scale experimental tank after ten(10) years and taken out used dry batteries from the tank. Corrosion of these dry batteries is shown in Photo 1. When we check the condition of corrosion of dry batteries in the tank as a whole, we found that metal jacket of used dry batteries were corroded but we can still read these letters printed on it.

Consequently, we found that batteries were not so significantly corroded when packed in garbages for ten(10) years.

Photo 2 shows corroded dry batteries taken out from upper layer, middle layer and lower layer, respectively. We found that metallic seal plate of positive terminal for most of the dry batteries were peeled off as corrosion proceeded. Since we used fresh dry batteries for this experiment, it is reasonably assumed that these batteries were electrolytically corroded at initial periods of burial, and thus metallic seal plates were peeled off.

Outsides of dry batteries were found to be corroded, mainly in the following way.

a) Metal jacket was corroded and both iron rust and garbages sticked to it.
b) Connection of seal plate and metal jacket was peeled off and corroded.
c) Whole surface of metallic bottom plate (negative terminal) was corroded.
d) Whole metal jacket was corroded and lost.

Most corrosions were observed only on the surface of dry batteries and inside of the battery was found to be little corroded.

Corrosion of dry batteries was found to be dependent on "condition of burying tank", "battery voltage" and "period" but it has not significantly proceeded in ten(10) years when we checked these dry batteries which were buried for that period. It is reasonably considered that it takes much longer than ten(10) years that dry batteries are significantly corroded when buried in landfill sites.

Photo 1 Dry batteries in mixture tank

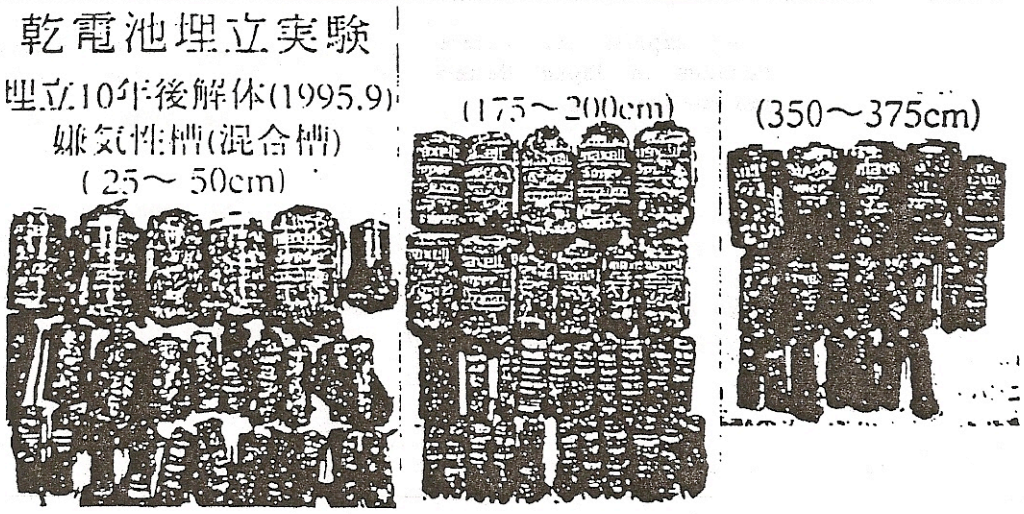
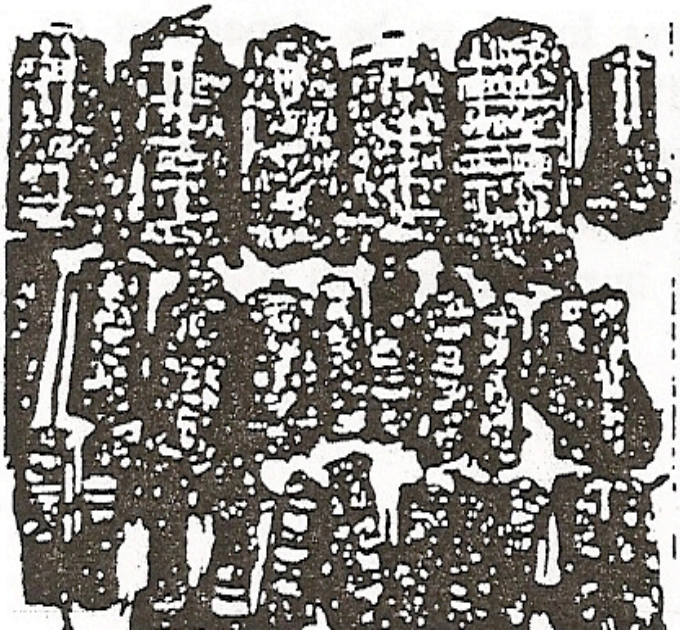


Photo 2 Corrosion of dry batteries in mixture tank

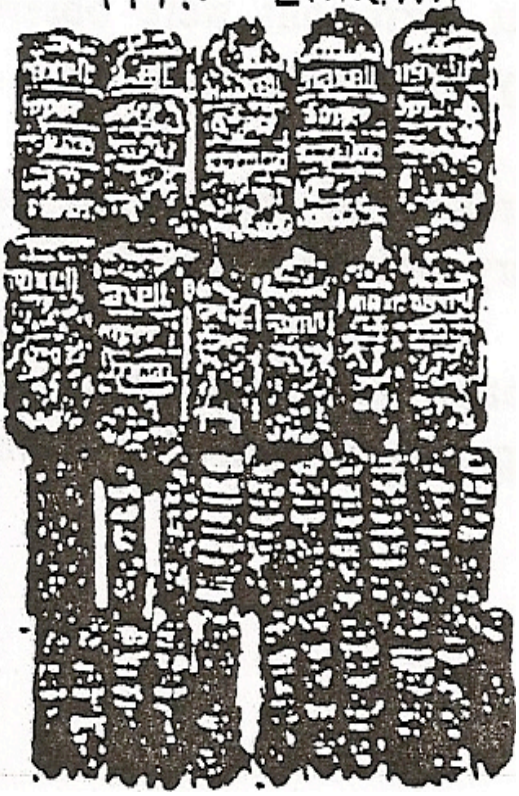
竪立10年後解体(1995.9)

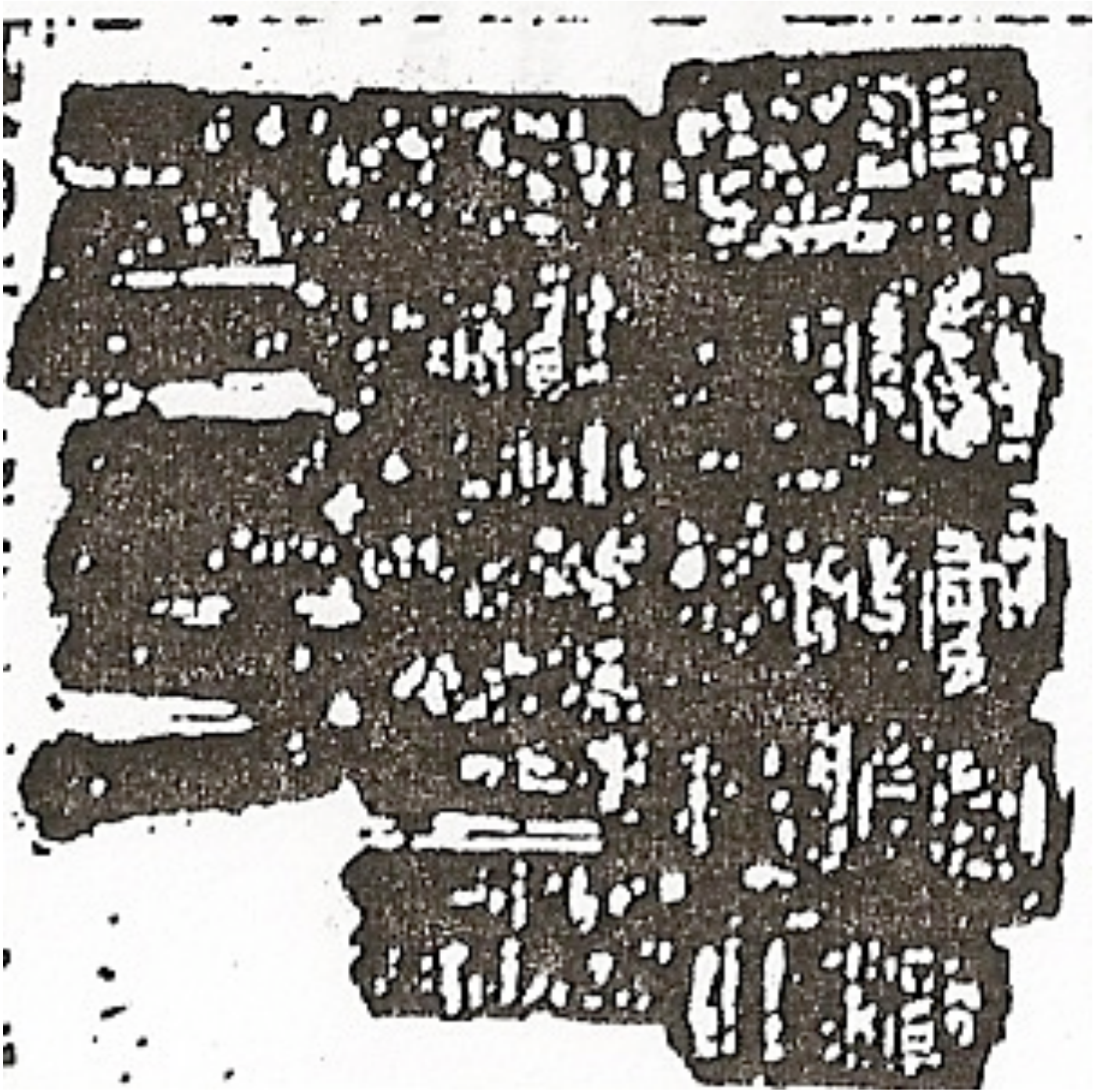
嫌気性槽(混合槽)

(25～ 50cm)



(175～200cm)





4 Conclusion

We have studied the behavior of mercury and corrosion of dry batteries when they are buried in landfill sites for ten(10) years. We have found the followings.

a) Corrosion of dry batteries has not significantly proceeded in ten(10) years (below our original estimation).
b) Amount of mercury escaped in the leachate and in the air in ten(10) years was found to be very small and the mercury seemed to be absorbed in the garbage and still remaining in the burying tank. Amount of mercury in the tank was found to have changed very little in these ten(10) years.

As a result, we are now studying the effect of used dry batteries containing mercury, when they are landfilled, in the following way.

a) To check if covering of the top surface and side surface of buried used batteries with high density polyethylene sheet (to prevent rainfall water from penetrating onto buried used batteries) is effective for better environmental protection.
b) To check the possible corrosion of used dry batteries and escape of mercury from them in longer period than ten(10) years.

We express our sincere thanks to the burial experiment committee of used dry batteries in Japan Battery and Appliance Industries Association for kind assistance and co-operation.