AN INVESTIGATION OF THE DEGRADATION OF SOME DRY CELL BATTERIES UNDER DOMESTIC WASTE LANDFILL CONDITIONS

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(Received March 14, 1978)

Summary

The corrosion of seven types of dry cell battery in landfill leachate at 50°C over a period of 100 days has been investigated. Generally aerobic conditions resulted in substantially faster corrosion than anaerobic conditions and fully charged batteries corroded more rapidly than partially discharged batteries. RM675 and RM401 mercury batteries corroded rapidly and in some cases visible exposure of mercury occurred within the 100 day period. MN1500 and silver—zinc cells corroded less rapidly and, since they contain only a relatively small proportion of mercury, no visible mercury exposure occurred in the 100 day period. VB18 nickel—cadmium battery cases were perforated through the positive terminal face during the tests. Extensive corrosion of the zinc cans of SP2 and HP7 zinc—carbon cells was also found.

Analyses of leachates used in the corrosion tests and from columns of refuse containing up to 25 ppm of mercury as battery contents showed levels of mercury below 1 ppm and generally below 0.1 ppm. Silver concentrations in leachates were below 4 ppb, cadmium concentrations below 10 ppb and nickel concentrations below 5 ppm. Concentrations of zinc and manganese were variable and pH dependent. Above pH 8 their concentrations were below 10 ppm but below pH 6 to 7 concentrations ranged from tens to hundreds of parts per million. Chloride was released to leachate from zinc—carbon batteries during the corrosion tests.

Introduction

A large proportion of the dry cell batteries marketed in the U.K. are ultimately deposited in landfill sites amongst other domestic wastes. These cells will then constitute a potential source of metals, especially mercury [1], which might contaminate leachates leaving the site. In order to assess the rate at which batteries might decay in landfill, and the extent to which they may release their metallic components to leachate, laboratory corrosion and leaching tests were carried out. A burial experiment was also carried out at a landfill site to assess the validity of the laboratory test results.

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Seven types of dry cell battery were selected for inclusion in the corrosion tests. These were cylindrical RM401 mercury cells, button type RM675 mercury cells, MN1500 alkaline manganese cells, HP7 zinc—carbon cells, SP2 zinc—carbon cells, button type VB18 nickel cadmium cells and 10L14 button type silver—zinc cells. The external dimensions of these cells are shown in Table 1.

TABLE 1

Dimensions of dry cell batteries studied

Type of dry cell	Diameter (mm)	Thickness or length (mm)
RM401 Cylindrical mercury	11.4	28.4
RM675 Button mercury	11.5	5.1
MN1500 Cylindrical alkaline—manganese	14.0	50.0
HP7 Cylindrical zinc—carbon	13.2	49.3
SP2 Cylindrical zinc—carbon	32.9	60.7
10L14 Button silver—zinc	11.5	5.1
VB18 Button nickel—cadmium	24.8	11.2
400DK* Button nickel—cadmium	25.0	13.9
90DKO* Tablet nickel—cadmium (oval not circular section)	25.6 × 14.1	5.7

*These types of cell were used only in the landfill burial experiment.

Mercury cells are widely used in electrical appliances such as hearing aids which require the high energy to volume ratio provided by these cells. They are of especial interest because of their mercury content which can be of the order of 35% by weight. The button and cylinder type cells are identical electrochemically but differ in the internal arrangement of their components and their container design. Basically the cells consist of a pellet of zinc—mercury amalgam comprising the anode and a mixture of mercuric oxide and graphite comprising the cathode. These are separated by an ion permeable membrane soaked in an alkaline electrolyte such as potassium hydroxide.

During discharge the zinc is oxidised to zinc oxide while the mercuric oxide is converted to mercury metal. The cell container is fabricated from nickel plated steel and this is usually covered by a plastic wrapper in the case of the cylindrical cells. The negative terminal button of the battery is separated from the battery case by a plastic grommet. In the button type cells the case constitutes the positive terminal while in the cylindrical cells a separate button set into the base of the battery constitutes the positive terminal.

Cylindrical alkaline manganese batteries are similar in construction to cylindrical mercury batteries. They can provide comparatively heavy currents and have good storage properties. The cathode of the cell consists of a high density mixture of manganese dioxide and graphite compressed into a cylinder to fit around the anode, which consists of a zinc powder paste with aqueous potassium hydroxide. These two electrodes are again separated by an alkali soaked ion permeable membrane. The cell is contained in an electroplated steel can and the negative and positive terminals are provided by buttons at each end of the cylindrical can. The steel can is covered in a thin plastic film which is, in turn, covered by a lacquered metal outer cover crimped over the battery. The products of the discharge reaction are zinc oxide and hydrated manganese(III) oxide. The batteries also contain ca. 1% by weight of mercury [1].

Historically, zinc—carbon batteries based on the Leclanché cell are the original dry cell battery. They find use in a wide variety of portable electrical appliances and their comparatively low cost allows them to compete with higher performance cells. Basically the cell consists of a zinc cup which constitutes the anode and which contains the cathode in the form of a mixture of graphite and manganese dioxide powder soaked in a solution of an electrolyte such as ammonium chloride. Zinc—carbon cells may also contain a small proportion of mercury in the form of $HgCl_2$. A central carbon rod makes contact between the cathode and a brass terminal button on top of the cell which is separated from the zinc cup by a washer. During discharge of the cell the zinc can is chemically converted to zinc oxide. The manganese dioxide is, at the same time, reduced to MnOOH or $Mn_2O_3 \cdot H_2O$, a hydrated manganese(III) oxide. In HP7 batteries the zinc-cup forms the outer case of the battery being protected only by a thin printed plastic wrapper. In the case of SP2 batteries there is a bitumen seal beneath the washer separating the zinc cup from the carbon rod and the cell is contained in a cardboard sleeve and printed metal outer case.

Nickel—cadmium batteries differ from the other types studied in that they are rechargeable and are secondary batteries rather than primary cells. They are most commonly used in calculators and the portable two-way radios used by the police and emergency services. Both cylindrical and button type batteries are available, although the button type are generally stacked in plastic cassettes for use in radios. The cell is made up from a stack of circular metal plates coated with microporous nickel sponge. These are alternately impregnated with cadmium or nickel hydroxide forming the anodes and

cathodes of the cell respectively. These anodic and cathode plates are soaked in electrolyte solution and separated by spacers in the form of thin plastic discs. The anodic plates are connected to the top face of the button which constitutes the negative terminal while the cathodic plates are connected to the rest of the battery case. The case and negative terminal faces are separated by a plastic or rubber grommet. In the charged state the battery contains cadmium metal and nickel(III) hydroxide (NiOOH) while in the discharged state it contains cadmium hydroxide and nickel(II) hydroxide (Ni(OH)$_2$).

Sales of silver—zinc batteries, mainly for use in electronic watches, are likely to increase substantially in future years [1]. Thus they were included in this study. These batteries are similar in appearance to button type mercury batteries and utilise the electrochemical reaction between zinc amalgam and a silver salt. As with RM675 mercury batteries, the battery case constitutes a positive terminal and a central button the negative terminal. These cells contain ca. 1% by weight of mercury [1], and the intrinsic value of their silver content promotes their recovery.

Experimental

The corrosion of specimens of each type of dry cell battery selected for study was investigated under four sets of experimental conditions. These test conditions involved the use of both charged and discharged batteries under both aerobic and anaerobic conditions. All the experiments were carried out at a temperature of 50°C, which represents the maximum likely to be encountered in the body of a landfill site, and samples of RM401 and MN1500 battery cases were also tested. After measurement of its initial voltage a specimen battery was placed in a flask and 400 ml of domestic waste leachate was added. This leachate was prepared by saturating a 50 kg aliquot of pulverised domestic waste with water for a period of weeks then draining off the liquid. The composition of the leachate is described in the tables which follow in the 'Results' section. The flasks were stoppered and a slow stream of compressed air or high purity nitrogen was respectively bubbled through the liquid or passed over the surface to maintain aerobic or anaerobic conditions. The specimen batteries were exposed to the leachate for 100 days after which time they were removed for examination, photographed and samples of the leachates taken for analysis.

In addition to the laboratory tests, samples of batteries were also placed in a lined trench at the Marcham domestic waste landfill site, Oxfordshire. These were then covered by a 1 metre layer of unpulverised domestic waste and ca. 25 cm of inert cover material. After seven months the site was excavated, the specimen batteries were recovered for examination and their condition recorded photographically.

In order to study the leaching of mercury from disintegrated batteries under model landfill conditions, columns were prepared containing samples

of mercury as dry cell contents in pulverised fresh domestic waste obtained from the Cambridgeshire site at Thriplow. The composition of this waste has been described elsewhere [2]. A 5-litre aspirator was fitted with a stopcock for draining and a bung and fermentation lock to close the neck. A 1 kg sample of waste was placed in the aspirator and the sample of battery contents under investigation distributed over this layer. A further 0.5 kg of waste was then added to the column and the whole saturated with 2 l of water. A nominal load of 10 ppm of mercury was to have been used but this was found to require samples of battery contents which were too small to handle conveniently. Consequently a nominal mercury to waste loading of 25 ppm w/w was used in three of the columns.

Four types of battery contents were used viz. charged RM401, discharged RM401, discharged MN1500 and discharged 10L14 silver—zinc cells. Samples of RM401 and MN1500 cell contents were taken in the form of transverse slices from which a segment of the appropriate weight was removed. Similar segments to those placed in the column were dissolved in nitric acid and analysed for metals. The results indicated that the mercury to waste load for RM401 and MN1500 cell contents was 25—30 ppm w/w. In the case of silver—zinc cells the contents of a whole single cell were used. Assuming the cell was 1% by weight mercury this gave a mercury to waste load of 13 ppm for the silver—zinc cell column. Estimated loadings of manganese and zinc from the battery contents are also given in the tables of data which follow in the results section.

After the saturated columns had stood at ambient temperature for 2 weeks 500 ml of leachate were drained from the column and returned to the top of the column. A 20 ml sample of leachate was then drained out to completely fill a glass sample bottle which was immediately closed by a ground glass stopper and sent for analysis [3]. This procedure was repeated after 4 weeks then the leachate was drained from the columns. Following this the columns were eluted at a rate of 5 cm of water per week (1,300 ml) and the liquid allowed to build up for 2 week intervals after which the column was drained and a leachate sample taken. This procedure was followed for a further period of 8 weeks after the initial 4 weeks under saturated quiescent conditions giving a total experiment duration of 3 months.

In addition to the contaminated columns two 'blank' columns were set up containing 1.5 kg of waste plus 2 l of water. These were allowed to stand for 5 weeks, and the leachate then drained out for analysis. The principal purpose of these 'blanks' was to assess the background concentrations of metals present in waste leachates.

The leachate samples were analysed for relevant metals, organic acids and organic mercury. Metal analyses were performed by atomic absorption spectrophotometry on acidified leachate solutions and organic acids and organic mercury analyses were carried out by gas chromatography. The detection limits varied and, for metals, they are indicated in the tables following in the "Results" section. Limits for detection of organic acids were 20 to 40 ppm and for organic mercury 1 ppm.

Battery corrosion results

(a) Laboratory test results

At the end of the 100 day test period the leachate in the aerobic flasks was found to be clear with large quantities of a red-brown deposit at the bottom of the flasks. Leachate from the anaerobic tests was also clear but was covered with a scum of oily appearance. The residue at the bottom of these flasks was initially of a greenish colour but turned brown on standing in air. Generally, this deposit appeared to arise from materials originally present in the leachate but in some cases it was in part due to corrosion products of the batteries themselves.

Photographs of the test batteries are reproduced in Appendix I (Fig. 1—12) and a qualitative assessment of the condition of each of the battery specimens after the 100 day corrosion test is given in Table 2, along with the initial cell voltages. Two important factors controlling the degree of corrosion are immediately apparent, namely the state of charge of the battery and whether conditions were aerobic or anaerobic. Aerobic conditions invariably result in more rapid or damaging corrosion than anaerobic conditions. Since conditions in the bulk of landfilled domestic waste eventually become anaerobic, this factor will tend to decrease the rate at which batteries corrode in landfill. Tests on the nickel plated steel battery casing material emphasised the difference between aerobic and anaerobic conditions. Complete corrosion of the steel occurred under aerobic conditions while little or no corrosion was apparent under anaerobic conditions.

The state of charge of the battery has a pronounced effect on the extent to which the positive terminal is attacked. Even discharged batteries can carry some residual charge which can contribute to the corrosion process. During complete discharge of the battery through the external circuit provided by ions in the leachate, the negative terminal experiences some cathodic protection while the positive terminal suffers enhanced corrosion. These effects are most apparent in the button type batteries where the battery case constitutes the positive terminal and in the HP7 zinc—carbon cells where the negative case was protected from external corrosion during the discharge process. Another factor which appeared to protect battery cases from corrosion was the presence of a lacquered outer case insulated from the battery as found in the MN1500 and SP2 type batteries.

Taking each type of battery in turn, the RM675 button type mercury cells were very susceptible to corrosion. The release of mercury was apparent even with discharged cells under anaerobic conditions. Complete failure of the casing of a charged battery occurred under aerobic or anaerobic conditions and it seems possible that a substantial portion of the mercury in RM675 batteries could be exposed within 1 year in a landfill site. RM401 cylinder type mercury batteries were a little more robust and a discharged cell under anaerobic conditions did not corrode significantly. However, under aerobic conditions, or when the batteries were charged, exposure of mercury did occur during the 100 day test period.

TABLE 2

Qualitative assessment of battery conditions after corrosion tests
(Photographs of the test batteries are reproduced in Appendix I, Fig. 1—12)

Battery type	Initial voltage*	Conditions of battery after 100 days	
		Anaerobic leachate*	Aerobic leachate*
MN1500 Charged	N$_2$ 1.556 Air 1.554	The centre button terminal (+ve) was totally corroded as was ca. 25% of the case. The plastic inner sleeve was intact.	In similar condition to the anaerobic test cell.
MN1500 Discharged	N$_2$ 1.108 Air 1.091	Partial corrosion of the centre button terminal (+ve). The case was unattacked.	In similar condition to the anaerobic test cell.
RM401 Charged	N$_2$ 1.477 Air 1.480	Complete corrosion of ca. 25% of the outer case (+ve) near the negative terminal end had occurred. The steel was corroded leaving two uncorroded layers of nickel plating.	Severe corrosion of the case occurred at the negative terminal end and exposed the contents. Globules of mercury were visible and the battery contents fell out during examination.
RM401 Discharged	N$_2$ 1.157 Air 1.136 and 0.102	No corrosion was apparent.	The cases of both batteries were severely corroded. The mild steel was corroded from both ends leaving a 'skin' of nickel plate which exposed mercury globules when removed.
RM675 Charged	N$_2$ 1.513 Air 1.513	The case (+ve) was severely corroded, especially at the edges where mercury was visible. The remnants of the outer case were easily removed exposing the battery contents.	The case (+ve) was severely corroded leaving only a fragile 'skin' of nickel plating. Slight pressure caused mercury to ooze from the cell.
RM575 Discharged	N$_2$ 1.351 Air 1.351	Slight etching of the negative terminal was apparent though the case was intact. However, firm pressure caused mercury to ooze from between the plastic grommet and the negative terminal.	Although apparently intact most of the steel case had corroded from the plating of nickel. Slight pressure caused mercury to ooze from the battery.

TABLE 2 (*continued*)

Battery type	Initial voltage*	Condition of battery after 100 days	
		Anaerobic leachate*	Aerobic leachate*
HP7 Zinc—carbon Charged	N$_2$ 1.65 Air 1.68	Brass +ve terminal cap completely corroded. The zinc case (−ve terminal) was largely unattacked.	Brass +ve terminal cap completely corroded. The zinc case was intact but tarnished.
HP7— Zinc—carbon Discharged	N$_2$ 0.69 Air 0.80	Brass +ve terminal cap completely corroded. The zinc can beneath the label was perforated over ca. 30% of its surface.	The zinc case was perforated over ca. 50% of its surface and the remainder was severely corroded.
SP2 Zinc—carbon Charged	N$_2$ 1.56 Air 1.57	Brass +ve terminal cap completely corroded. Outer case unattacked, zinc can slightly corroded, perforation occurred from inside.	Brass +ve terminal cap completely corroded. The bitumen seal leaked from the end of the cell. The outer case was corroded only at the seam. The inner zinc case was perforated from inside.
SP2 Zinc—carbon Discharged	N$_2$ 0.36 Air 0.36	Brass +ve terminal cap completely corroded. Outer case uncorroded but only the base of the inner zinc can remained intact.	Brass +ve terminal cap completely corroded. Outer case corroded at seam. Only the base of the zinc can remained intact.
VB18 Nickel—cadmium Charged	N$_2$ 1.294 Air 1.270	Positive terminal pitted and removal of corrosion product exposed interior of cell. No corrosion of −ve terminal.	A large area of +ve terminal completely corroded exposing the cell interior. Attack of −ve terminal around the edges.
VB18 Nickel—cadmium Discharged	N$_2$ 1.151 Air 1.118	Similar but slightly less extensive corrosion compared to charged cell.	Similar but slightly less extensive corrosion compared to charged cell.
Silver—zinc Charged	N$_2$ 1.582 Air 1.582	Corrosion occurred around the edges of the positive casing producing a pit ca. 1 mm in diameter. Otherwise the battery was intact.	Severe corrosion of the case (+ve) occurred especially around the rim. The outer layer of nickel plating was easily removed to expose the battery contents.
Silver—zinc Discharged	N$_2$ 0.012 Air 0.062 and 0.178	No apparent corrosion had occurred	One cell appeared uncorroded while the other was only slightly corroded on the side edges of the casing.

TABLE 2 (*continued*)

Battery type	Initial voltage*	Conditions of battery over 100 days	
		Anaerobic leachate*	Aerobic leachate*
Samples of MN1500 and RM401 battery casing	—	Both samples were apparently uncorroded.	Both samples were completely corroded leaving only rust flakes and the thin nickel plating.

* Anaerobic leachate was maintained under a high purity nitrogen atmosphere; test cell voltages are indicated by 'N$_2$'.
Aerobic leachate conditions were maintained by bubbling compressed air through the samples; test cell voltages are indicated by 'Air'.

Silver—zinc batteries were less prone to corrosion than the mercury button cells and only the charged battery under aerobic conditions showed complete failure of the casing. Under the other conditions studied no major damage to the battery case was found.

Alkaline manganese (MN1500) batteries also proved to be more corrosion resistant than the mercury batteries. The outer lacquered metal shell, insulated from the charged metal battery casing, appeared to offer considerable protection against corrosion. Only charged MN1500 batteries were sufficiently corroded to expose a small part of their contents beneath the positive terminal. Complete failure of the casing of discharged MN1500 batteries in anaerobic landfill seems likely to take a number of years.

The zinc—carbon cells differed from the others studied in that the zinc can of the battery was cathodically protected from external corrosion during discharge. As a result the zinc cans of discharged cells, which had already been corroded from the inside, were more prone to failure than those of the charged cells. The brass positive terminal button of these batteries corroded away under all the conditions studied but only exposed an inert carbon rod. The outer casing of the SP2 batteries provided good containment of the cell contents after complete failure of the zinc can. However, the plastic wrapper of the HP7 batteries was far less mechanically strong and would start to lift off the cell contents following complete corrosion of the zinc can. Degradation and break-up of HP7 batteries in landfill thus seems possible within a period of a year or so while the outer case of SP2 cells is likely to contain the cell contents for somewhat longer.

Corrosion of the nickel—cadmium (VB18) batteries resulted in perforation of the battery case under all the conditions studied. Perforation occurred on the flat positive terminal face but this did not result in the extensive exposure of the cell contents. More damage was sustained by the charged cells under aerobic conditions than by discharged cells under anaerobic conditions. The initial voltage of both charged and discharged VB18 batteries was similar and this undoubtedly made a significant contribution to the corrosion process.

Among the dry cell batteries studied, button type mercury cells and HP7 zinc—carbon cells are likely to break up the most rapidly in anaerobic landfill and expose their cell contents. The outer cases of SP2 zinc—carbon cells will delay their disintegration considerably compared to HP7 batteries. Silver—zinc and nickel—cadmium batteries are prone to corrosion though the plastic cassettes in which the latter are commonly packed will delay disintegration considerably. Alkaline manganese MN1500 batteries appeared to be the most robust of those studied and, apart from attack of the positive terminal button were comparatively inert to corrosion.

(b) Landfill burial test results

These results may be compared with those obtained in the burial experiment and photographs of the test batteries recovered are reproduced in Appendix II (Fig. 13—24). After 7 months burial in anaerobic landfill SP2 and MN1500 batteries were still intact and largely undamaged, except for corrosion of the positive terminal buttons of charged batteries. RM401 mercury cells were corroded and the cases perforated in places, although no exposure of mercury was apparent. The zinc cans of charged HP7 batteries were perforated over ca. 10—30% of their surface and a thin zinc foil remained over the rest of the battery, whilst the zinc cans of discharged HP7 batteries were generally perforated over more than 50% of the surface. The wrappers and rigidity of the cell contents appeared to have prevented disintegration from occurring to a significant extent. The nickel—cadmium button cells recovered were generally in good condition and showed little sign of damage. No button type mercury or silver—zinc cells were recovered though this seems more likely to be due to the difficulty of locating them in decomposing waste than to their complete disintegration.

(c) General discussion of corrosion test results

Based on these observations it seems that the corrosion of batteries over 7 months in landfill occurs to a somewhat lesser extent than over 3 months immersion in anaerobic leachate. It seems, therefore, that the laboratory test conditions produce an accelerated rate of corrosion, perhaps of the order of 5 times faster than in landfill. This could be due to a number of factors. The test temperature of 50°C, which was maintained for 3 months, may not adequately reflect the temperature of the landfill which probably rises from ambient to a transient peak of 50°C in the first six months then slowly declines to 5 to 10°C above ambient. In the laboratory tests the batteries were completely immersed in leachate while in landfill saturated conditions are not generally found. Thus, in landfill, a conducting pathway between the battery terminals may only exist intermittently if at all. This reduces the ability of residual charge in the battery to contribute effectively to the corrosion process. One final observation was that the nickel plating on the cases of RM401 mercury batteries was corroded in the landfill but left largely intact in the laboratory tests.

Leachate analyses results

The analytical data obtained from samples of leachate removed from the flasks following the 100 day corrosion tests are presented in Tables 3, 4, 5 and 6. Separate batches of leachate were used for tests on the zinc—carbon and nickel—cadmium batteries. These two batches proved to have a lower organic content than that used for tests on the mercury, alkaline—manganese and silver—zinc batteries. The metal contents of settled leachate samples from each batch are shown in the appropriate tables.

The mercury concentrations found in the leachate samples were 0.05 ppm or below except for one value of 0.81 ppm found for a charged RM401 battery under aerobic conditions. To place this figure in perspective it represents

TABLE 3

Mercury, alkaline—manganese and silver—zinc batteries. Analytical data for leachates from anaerobic corrosion tests

Analyses were performed on the supernatant after the leachate had stood for 1 week to settle. <, less than figure quoted, —, not determined.

Battery type	Final pH	Leachate analyses (w/v, ppm)					Organic acid total* (v/v, ppm)	Chloride (w/v, ppm)
		Hg***	Zn	Mn	Ni	Ag		
Test leachate	6.0	<0.01	50	93	1.6	—	9,615**	660
MN1500 Charged	7.2	0.050	—	—	1.4	—	14,870	830
MN1500 Discharged	6.9	<0.01	5.4	74	2.5	—	14,285	780
RM401 Charged	6.3	<0.01	2.4	88	2.5	—	12,230	760
RM401 Discharged	5.7	<0.01	—	—	3.2	—	14,725	840
RM675 Charged	5.7	<0.05	120	180	3.5	—	15,240	980
RM675 Discharged	5.4	<0.01	—	—	2.0	—	13,480	790
Silver—zinc Charged	5.5	<0.01	51	110	2.2	<0.04	13,030	780
Silver—zinc Discharged	5.5	0.005	—	—	2.0	<0.04	16,226	980
Samples of MN1500 and RM401 casing	5.9	0.007	—	—	2.1	—	13,100	910

*, **, *** — Key follows Table 4.

TABLE 4

Mercury, alkaline—manganese and silver—zinc batteries. Analytical data for leachates from aerobic corrosion tests

Analyses were performed on the supernatant after the leachate had stood for 1 week to settle. <, less than figure quoted, —, not determined

Battery type	Final pH	Leachate analyses (w/v, ppm)					Organic acid total* (v/v, ppm)	Chloride (w/v, ppm)
		Hg***	Zn	Mn	Ni	Ag		
MN1500 Charged	8.0	<0.01	0.30	8.4	1.7	—	16,125	1,470
MN1500 Discharged	8.8	<0.01	0.50	0.06	1.5	—	4,430	780
RM401 Charged	8.0	0.81	0.17	5.8	1.3	—	9,610	840
RM401 Discharged	7.8	0.013	0.22	0.32	0.7	—	9,930	750
RM675 Charged	5.2	<0.01	38	130	2.4	—	12,545	820
RM675 Discharged	4.8	0.011	43	100	1.7	—	13,675	850
Silver—zinc Charged	4.8	<0.01	37	110	2.7	<0.04	11,880	800
Silver—zinc Discharged	5.0	<0.01	42	100	1.7	<0.04	12,980	870
Samples of MN1500 and RM401 casing	5.5	<0.01	—	—	78	—	11,230	780

*(a) Figure for organic acids is total of acetic, propionic, butyric, iso-butyric, valeric and iso-valeric acid concentrations.
(b) Average total organic acid was 12,755 ppm comprised as follows:

Acid	v/v ppm concentration	% of total
Acetic	6,688	52.4
Propionic	909	7.1
Butyric	4,212	33.0
Iso-butyric	524	4.1
Valeric	302	2.4
Iso-valeric	120	0.9
	12,755	99.9

The composition of a sample of the leachate used in the tests and stored in a sealed container for 3 months with no added material was as follows:

TABLE 4 (*continued*)

Acid	v/v ppm concentrations	% of total
Acetic	5,955	61.9
Propionic	765	7.9
Butyric	2,220	23.1
Iso-butyric	450	4.7
Valeric	160	1.7
Iso-valeric	65	0.7
	9,615	100.0

**This sample was abnormally low in acetic (680 vpm), and propionic (190 vpm) acids. Levels of the other acids were fairly typical.
***Estimated maximum potential mercury concentrations in leachate are RM401, 10,000 ppm; MN1500, 580 ppm; RM675, 1900 ppm; and silver—zinc cells, 50 ppm.

TABLE 5

Zinc—carbon and nickel—cadmium batteries. Analytical data for leachates from anaerobic corrosion tests

—, not determined; <, less than the figure quoted

Battery type	Final pH	Leachate analyses (w/v, ppm)*						
		Hg	Zn	Mn	Ni	Cd	TOC	Cl
HP7 Zinc—carbon Charged	8.1	<0.0001	7.7	3.0	—	—	1,100	867
HP7 Zinc—carbon Discharged	7.8	0.0009	54	82	—	—	1,200	2,920
SP2 Zinc—carbon Charged	7.6	0.0011	120	4.6	—	—	1,200	1,330
SP2 Zinc—carbon Discharged	7.0	0.001	620	240	—	—	970	5,990
VB18 Nickel—cadmium Charged	—	—	—	0.1	0.7	<0.01	670	—
VB18 Nickel—cadmium Discharged	—	—	—	0.2	1.0	<0.01	660	—

*Leachates were allowed to settle under gravity for 2 hours prior to analysis of the supernatant.

TABLE 6

Zinc—carbon and nickel—cadmium batteries. Analytical data for leachates from aerobic corrosion tests

—, not determined; <, less than the figure quoted

Battery type	Final pH	Leachate analyses (w/v, ppm)*						
		Hg	Zn	Mn	Ni	Cd	TOC	Cl
HP7 Zinc—carbon Charged	7.1	0.0013	63	10	—	—	1,400	1,86(
HP7 Zinc—carbon Discharged	6.9	0.0143	190	10	—	—	340	3,36(
SP2 Zinc—carbon Charged	7.3	0.0032	160	18	—	—	1,500	4,88(
SP2 Zinc—carbon Discharged	6.3	0.002	910	180	—	—	1,100	10,38(
VB18 Nickel—cadmium Charged	—	—	—	<0.05	0.4	<0.01	260	—
VB18 Nickel—cadmium Discharged	—	—	—	0.05	0.3	<0.01	240	—
Tables 4 and 5 leachates								
Nickel—cadmium test	—	—	—	0.4	0.2	<0.01	190	—
Zinc—carbon test	7.8	0.0003	0.64	0.31	—	—	350	45!

*Leachates were allowed to settle under gravity for 2 hours prior to analysis of the supernatant.

0.325 mg of mercury in 400 ml of leachate or less than 0.01% of the mercury originally present in a battery whose case failed, exposing metallic mercury. It would seem, therefore, that the presence of exposed mercury from dry cells does not necessarily mean that a significant proportion will pass into solution. In addition to the low solubility of mercury itself, any dissolved mercury in anaerobic leachate is likely to be precipitated as the sulphide or adsorbed on the iron oxide—hydroxide gels which from in leachate. These mechanisms apparently combine to maintain mercury concentrations in leachate at the part per billion level in most cases.

Levels of nickel in the leachate, which could arise from the nickel plating of the battery cases, were generally low and in the range 0.3—0.4 ppm. A value of 78 ppm was obtained from the aerobic test cell containing battery cases alone although the anaerobic test cell containing cases only gave a value of 2.1 ppm nickel. Thus it seems that nickel concentrations in leachate contacting corroded batteries of the type studied will generally be below ca. 5 ppm.

Levels of zinc in the leachate samples ranged from 0.17 to 910 ppm. Concentrations below 1 ppm were generally associated with a leachate pH of ca. 8 or higher while high zinc concentrations generally corresponded with lower pH values. The highest observed zinc concentration of 910 ppm arose from a discharged SP2 battery in aerobic leachate at pH 6.3 and represented the dissolution of ca. 2.8% of the zinc originally present in the battery. At the other extreme only ca. 0.07% of the zinc originally present in a charged HP7 battery dissolved in anaerobic leachate at pH 8.1. Taken as a whole these results suggest that zinc—carbon cells could, under some conditions, constitute a significant source of zinc in landfill leachate. (See for example ref. 4d.)

As was the case for zinc, manganese concentrations in the leachates were highly variable and pH dependent, ranging from 0.06 to 240 ppm in the pH range 4.8 to 8.8. At a given pH, manganese levels in anaerobic leachate contacting discharged zinc—carbon batteries were generally substantially higher than from the other batteries studied. Chloride levels in leachates contacting discharged zinc—carbon batteries were also very high, especially where aerobic conditions prevailed. Thus zinc—carbon batteries appear to provide a potential source of manganese and chloride, as well as zinc and ammonium ions, in landfill leachate.

Silver concentrations in leachates contacting silver zinc batteries were below a detection limit of 0.04 ppm and cadmium concentrations in leachate contacting nickel—cadmium batteries were below a detection limit of 0.01 ppm. The chloride content of leachate would probably be effective in precipitating any silver which did dissolve from silver zinc batteries. The presence of sulphide in anaerobic leachate would also serve to precipitate most metals which might dissolve from dry cell batteries. No obvious correlation emerged between the metal concentrations found in leachate and its organic content.

Column leaching results

The analytical data for the column leachates are summarised in Tables 7 and 8. The total organic carbon (TOC) and organic acid analyses vary considerably and indicate that the extent of microbial degradation of waste components varies from column to column. This may result from differences in the putrescibles content of the waste samples or differences in their viable microbial populations. However, the results clearly indicate an accumulation of organic acids in the leachate over the 4 week period of quiescent conditions.

TABLE 7

Analytical data for leaching tests on refuse
Key: —, not determined; <, less than level quoted; N.D., none detected (i.e. less than 1 ppm organic mercury)

Battery type	Time of sample weeks	Analyses of leachate (w/v, ppm)				Organic acids (v/v, ppm)**	Organic mercury
		Hg	Zn	Mn	TOC		
Charged RM401*	2	0.01	3.9	3.0	1,200	N.D.	—
	4	0.01	1.6	41	2,000	N.D.	N.D.
	6	<0.01	0.46	27	3,700	A320; P115; IB40	N.D.
	8	0.01	0.48	23	1,600	N.D.	—
	10	<0.01	0.30	11	520	N.D.	—
	12	<0.01	0.28	16	630	N.D.	N.D.
Discharged RM401*	2	0.006	1.8	12	1,100	N.D.	—
	4	<0.01	0.6	22	1,400	A3205; P300; B240; IV20	N.D.
	6	<0.01	0.96	15	1,400	A2835; P380; B405; IB60; IV50	N.D.
	8	0.051	4.7	11	440	N.D.	—
	12	0.01	0.48	6.8	170	N.D.	N.D.
Analyses of leachates from uncontaminated waste	I 5	<0.018	1.0	22	3,500	A530; P430	N.D.
		(Ni, 0.9 ppm; Ag, <0.04 ppm; Cl⁻ 1,650 ppm)					
	II 5	<0.01	0.58	9.7	2,000	A N.D.; P155	—
		(Ni, 0.9 ppm; Ag, <0.04 ppm; Cl⁻ 1,280 ppm)					

*Metal to waste loads (w/w, ppm): Hg 26, Zn 12, Mn 3.8.
**Organic acids: A, acetic; P, propionic; B, butyric; V, valeric; IB, iso-butyric; IV, iso-valeric.

Subsequent elution of the columns dilutes the leachate and results in a successive decrease in organic acid and organic carbon concentrations.

The results from the 'blank' columns of uncontaminated waste show comparatively low organic acid concentrations although the TOC concentrations are broadly comparable with those in leachates from the contaminated columns. Levels of zinc and manganese in the leachates from the uncontaminated columns were broadly comparable with those in leachates from the contaminated columns and no silver, mercury, or organic mercury were detected in leachates from the uncontaminated 'blank' columns.

Analyses of the leachates from the contaminated columns for metals revealed no particularly high concentrations. The columns containing RM401 battery contents gave leachates whose zinc or manganese content was only occasionally higher than that from the 'blanks' (I and II in Table 6) and no organic mercury was detected. Inorganic mercury concentrations were generally 0.01 ppm or less except for one value of 0.05 ppm. The potential maximum metal concentrations in leachate assuming release of all the metal in the

TABLE 8

Analytical data for leaching tests on refuse
—, not determined; <, less than level quoted; N.D., none detected (i.e. less than 1 ppm organic mercury)

Battery type	Time of sample weeks	Analyses of leachate (w/v, ppm)					Organic acids (v/v, ppm)***	Organic mercury†
		Hg	Zn	Mn	Ag	TOC		
Discharged MN1500*	2	0.01	2.0	2.8	—	1,400	N.D.	—
	4	0.01	0.6	19	—	1,300	A3645; P375; B265	N.D.
	6	<0.01	1.1	8.8	—	820	N.D.	N.D.
	8	<0.01	0.74	4.0	—	680	N.D.	—
	10	<0.01	0.62	7.3	—	410	N.D.	—
	12	<0.01	0.94	7.1	—	210	N.D.	N.D.
Discharged silver—zinc**	2	0.018	1.5	—	<0.04	2,100	N.D.	—
	4	0.088	0.5	—	<0.04	2,200	A1715; P365; B315	N.D.
	6	0.016	1.6	—	<0.04	1,200	N.D.	N.D.
	8	<0.01	0.76	—	<0.04	640	N.D.	—
	10	<0.01	0.48	—	<0.04	310	N.D.	—
	12	0.37	0.50	—	<0.04	176	N.D.	N.D.
Burial test leachate	28	<0.0001	0.75	12	—	3,100	Cd, <0.05; Cl, 1,300 ppm	

*Metal to waste loads (w/w, ppm): Hg 30, Zn 280, Mn 300.
**Mercury to waste load (w/w, ppm): 13.
***Organic acids: A, acetic; P, propionic; B, butyric; V, valeric; IB, isobutyric; IV, isovaleric.
†Organic mercury analyses were carried out by gas chromatography against diethylmercury, di-n-propylmercury and methylmercury chloride standards. Detection limit 1 ppm.

first 4 week period are (for RM401 battery contents) Hg, 20 ppm; Zn, 9 ppm; Mn, 2.9 ppm. Thus the observed concentrations of mercury are all 2 to 3 orders of magnitude less than the possible maximum.

Leachate analyses for the column containing MN1500 battery contents were generally similar to those for the RM401 battery contents columns (Table 8). Mercury concentrations were again three orders of magnitude less than the hypothetical maximum of 23 ppm after 4 weeks. However, concentrations of zinc and manganese were not significantly different from those observed for the RM401 columns, despite the much higher manganese and zinc to waste loadings used in the MN1500 column. Thus, although some of the zinc and manganese may be leached from the battery contents over the period studied, the leachate concentrations produced by the low metal to waste load from RM401 cell contents are of comparable magnitude to those produced by the higher metal to waste load from MN1500 cell contents.

The silver—zinc cell contents column (Table 8) had the lowest mercury to waste loading (13 ppm) of all the columns, but produced the highest mercury concentrations. The hypothetical maximum concentration of mercury

attainable in leachate after 4 weeks is 10 ppm. The observed figure of 0.088 ppm after 4 weeks is two orders of magnitude lower but the concentration of 0.37 ppm after 12 weeks is much higher than would be expected from the other results. The reason for this high figure is uncertain and it may be a spurious result of little significance. However, to place it in perspective, the mercury concentrations in leachate from other columns correspond with removal of less than 1% of the added mercury over the 12 week experimental period. The mercury concentrations in leachate from the silver—zinc cell column correspond with the removal of 1 to $1\frac{1}{2}$% of the added mercury up to week 10 and removal of 5% added mercury between weeks 10 and 12. Concentrations of zinc in the leachate from the silver—zinc cell column are similar to those in leachate from the other columns and no silver was detected. The high chloride concentration in most leachates will probably be effective in precipitating trace quantities of silver ions.

Taking the leachate analyses as a whole there does not seem to be any significant correlation between the TOC or organic acid levels and the concentrations of the metal ions investigated. Thus there is no indication from these experiments that the leached metals are strongly associated with the organic matter content of the leachate. Broadly speaking the concentrations of zinc and manganese in the leachate did not decrease during the elution phase of the experiment, unlike the TOC levels. This would seem to indicate that the concentrations of these metals arise from a continuous leaching process rather than from a fairly complete initial release to the leachate during the 4 week equilibration period.

Conclusions

The laboratory corrosion tests indicate that 100 days immersion in aerated domestic waste leachate may result in perforation of the casing of the dry cell batteries studied. The most robust batteries were MN1500 alkaline—manganese and VB18 nickel—cadmium cells which only suffered penetration at the positive terminal. The least robust were HP7 zinc—carbon batteries in which the bulk of the ziic casing was corroded. The corrosion process occurred less rapidly under anaerobic conditions but was accelerated by residual charge in the cell, except where the case was cathodically protected as for zinc carbon cells.

Batteries recovered from a landfill site after 7 months of burial were somewhat less heavily corroded than those exposed to anaerobic leachate for 3 months in the laboratory. It would seem, therefore, that the laboratory tests exaggerate the corrosion rate by a factor of perhaps 5. However, a wide variation in rates of corrosion in landfill is to be expected depending on the local conditions in which a battery has been deposited.

Analyses of the leachate from the corrosion tests showed that only a very small proportion, if any, of the mercury, cadmium, nickel or silver present in dry cell batteries was dissolved by the leachate. More significant amounts of zinc or manganese were dissolved, especially from zinc—carbon cells, although

zinc and manganese concentrations were substantially reduced in leachates of pH 8 and above. Chloride also dissolved into leachate from zinc—carbon cells in significant amounts.

Although there were indications that zinc and manganese were dissolved by leachate, the concentrations of these elements in leachate from wastes contaminated with additional battery contents were not significantly higher than in leachate from uncontaminated wastes. Mercury concentrations in leachate from domestic wastes containing about 10 times the normal mercury load of ca. 2 ppm [1], and 5 times the recommended limit [1] of 4 mg/kg of landfill material, did not generally exceed 0.01 ppm. Again, contamination of domestic wastes with additional battery contents did not give rise to a significant increase in the leachate mercury concentration.

The behaviour of metals in landfill has also been studied in field and pilot scale work [4], and the findings described here are in accord with those of field investigations at sites where batteries and mercury containing wastes have been deposited. These field studies have shown that, although zinc and manganese may be leached from large deposits of Leclanché cell wastes [4d], there is no evidence that mercury is leached from landfilled material to any significant extent [4a] or that organo-mercury compounds are formed. Both the laboratory and field investigations indicate that, provided they are well mixed with household wastes and recommended [1] disposal practices [4] are employed, the presence of domestic arisings of primary dry cell batteries in landfill presents no special threat to groundwater quality.

References

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2 K. Knox and J.R. Newton, Study of Landfill Disposal of Acid Tars and Phenol Bearing Lime Sludges. Part I. WLR Report No. 19, Water Research Centre, Stevenage, January, 1976.
3 C.J. Jones and P.J. McGugan, Evaporation of Mercury from Aqueous Media, Journal of Hazardous Materials, 2 (1977/78) 253.
4 See WLR Technical Note Series especially:
(a) J.D. Mather and A. Parker, Report on Investigations into the Fate of Mercury Contained in Lamps and Batteries Incorporated in Domestic Refuse, WLR No. 12, Hazardous Materials Service, Harwell Laboratory, 1976.
(b) J.D. Mather and A. Parker, The Disposal of Industrial and Domestic Waste to a Landfill Overlying Lower Chalk. WLR No. 18, Hazardous Materials Service, Harwell Laboratory, March 1977.
(c) J.R. Newton, Pilot Scale Experiments on Leaching from Landfills. III Leaching of Hazardous Wastes. WLR No. 51, Water Research Centre, Stevenage, September, 1977.
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APPENDIX I. Photographs of dry cell batteries from laboratory corrosion tests (Figs. 1—12)

CELL 1   CELL 2   CELL 10   CELL 11

DEAERATED   AERATED
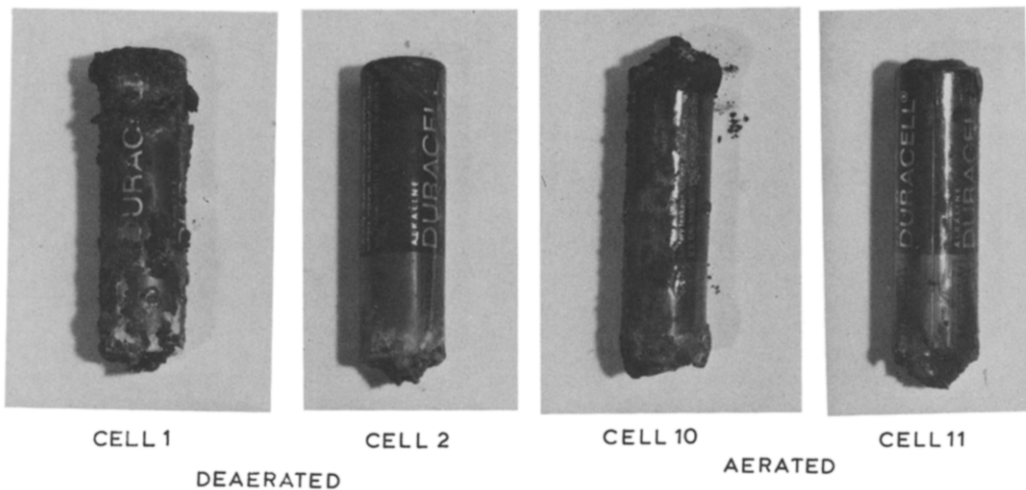
Fig. 1. MN1500 alkaline—manganese batteries. Cells 1 and 10 were charged, cells 2 and 11 discharged.

CELL 3   CELL 4

DEAERATED

CELL 12   A   CELL 13   B

AERATED
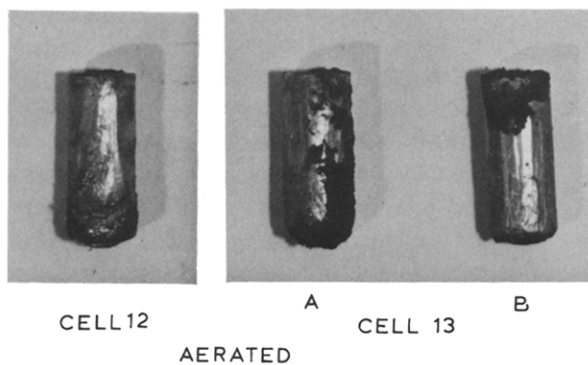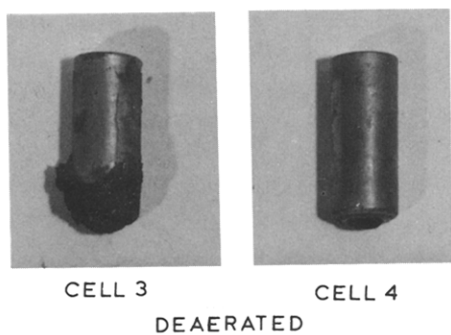
Fig. 2. RM401 mercury batteries. Cells 3 and 12 were charged, cells 4 and 13 discharged.
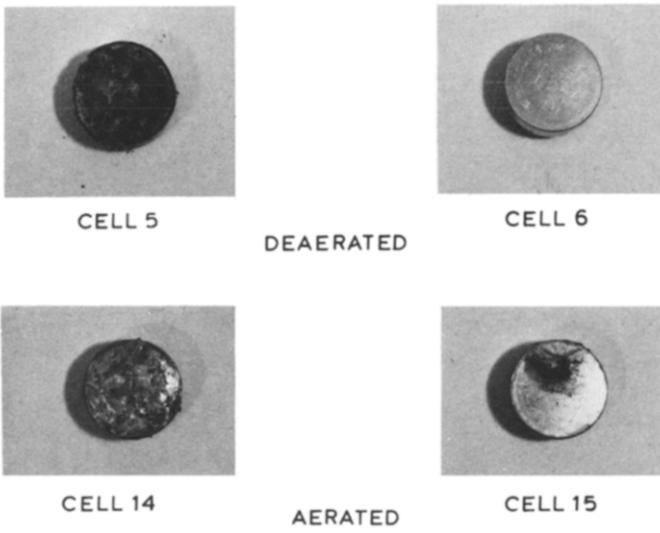
Fig. 3. RM675 mercury batteries. Cells 5 and 14 were charged, cells 6 and 15 discharged. The positive terminal face is shown.
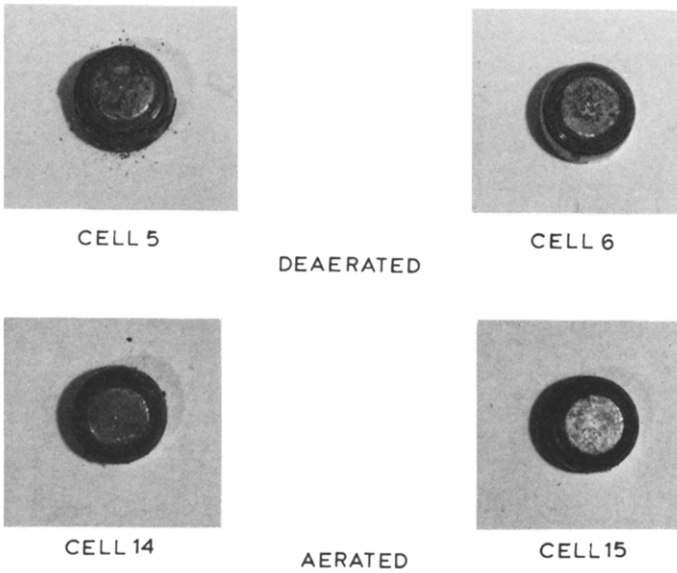
Fig. 4. RM675 mercury batteries. Cells 5 and 14 were charged, cells 6 and 15 discharged. The negative terminal button is shown.

CELL 7   CELL 8

DEAERATED

CELL 16   A   CELL 17   B

AERATED
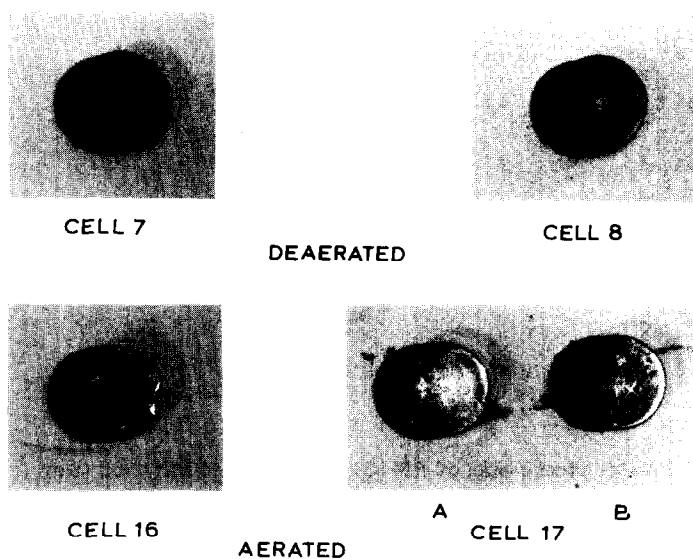
Fig. 5. 10L14 silver—zinc batteries. Cells 7 and 16 were charged, cells 8 and 17 discharged. The positive terminal face is shown.

CELL 7   CELL 8

DEAERATED

CELL 16   A   CELL 17   B
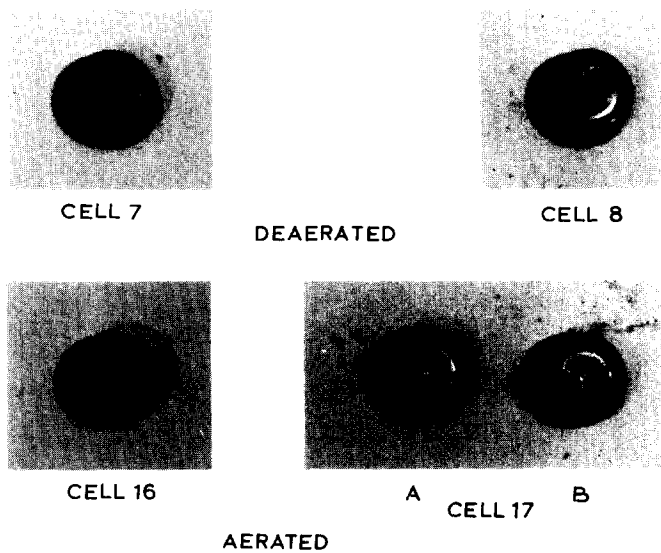
AERATED

Fig. 6. 10L14 silver—zinc batteries. Cells 7 and 16 were charged, cells 8 and 17 discharged. The negative terminal button is shown.
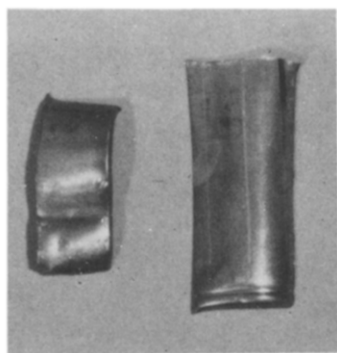
CELL 9
DEAERATED
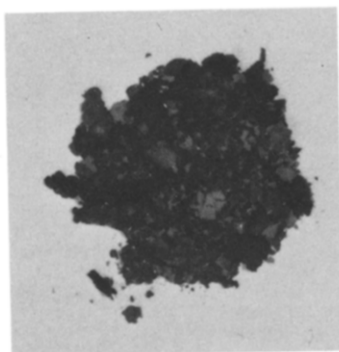
CELL 18
AERATED

Fig. 7. Samples of the nickel plated steel casing of RM401 (top left) and MN1500 (top right) batteries.

CELL 19

CELL 20

DEAERATED
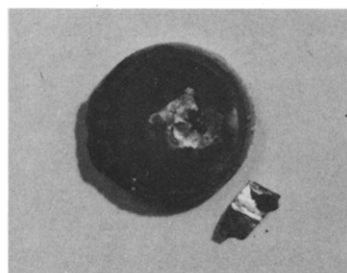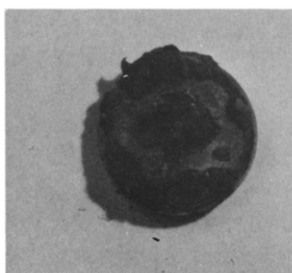
CELL 21

CELL 22

AERATED

Fig. 8. VB18 nickel—cadmium batteries. Cells 19 and 21 were charged, cells 20 and 22 discharged. The positive terminal face is shown prior to cleaning.

CELL 19   CELL 20

DEAERATED

CELL 21   CELL 22
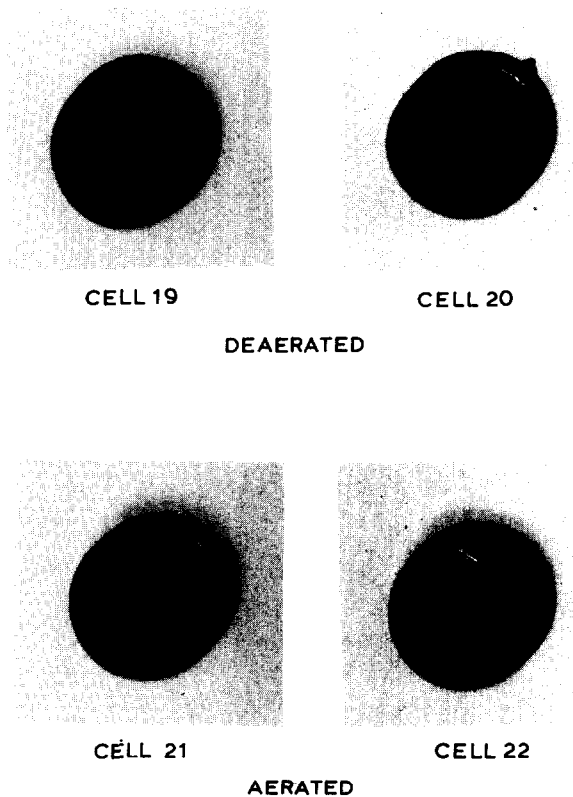
AERATED

Fig. 9. VB18 nickel—cadmium batteries. Cells 19 and 21 were charged, cells 20 and 22 discharged. The positive terminal face is shown after cleaning.

CELL 23   CELL 24

DEAERATED
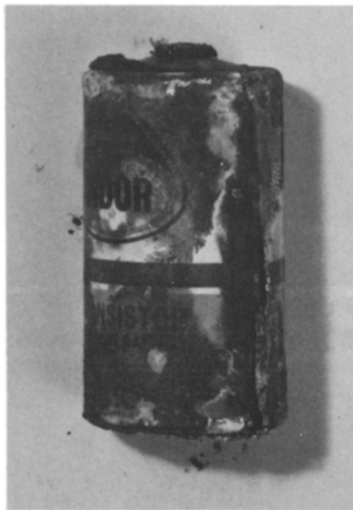
CELL 25   CELL 26

AERATED

Fig. 10. SP2 zinc—carbon batteries. Cells 23 and 25 were charged, cells 24 and 26 discharged. A side view is shown.

Fig. 12. HP7 zinc—carbon batteries. Cells 27 and 29 were charged, cells 28 and 30 discharged.
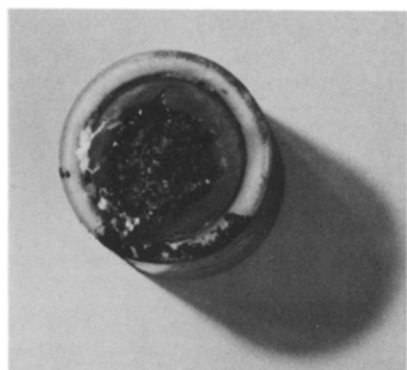
CELL 23   CELL 24
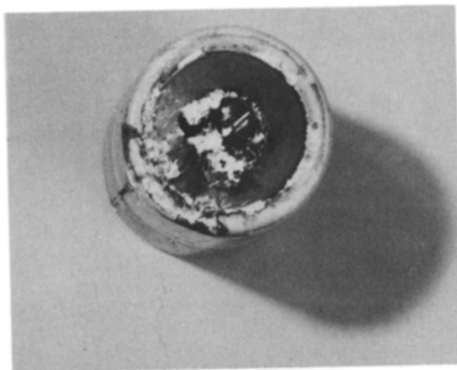
DEAERATED
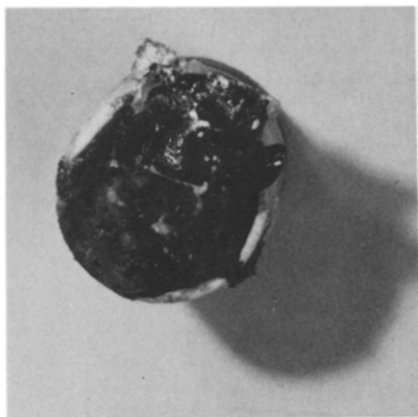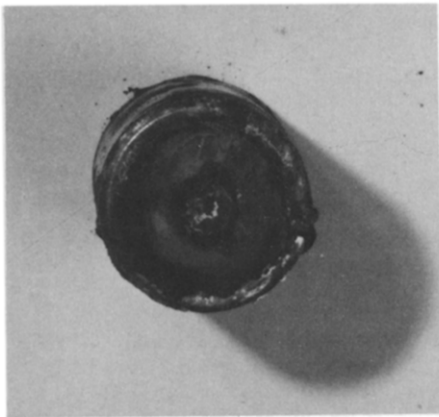
CELL 25   CELL 26

AERATED

Fig. 11. SP2 zinc—carbon batteries. Cells 23 and 25 were charged, cells 24 and 26 discharged. The positive terminal button is shown.

CELL 27   CELL 28   CELL 29   CELL 30
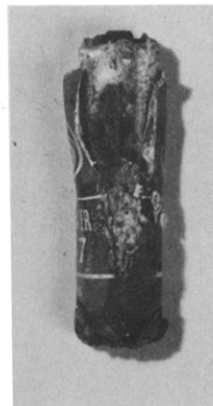
DEAERATED   AERATED

APPENDIX II. Photographs of dry cell batteries recovered from the landfill burial experiment (Figs. 13—24)
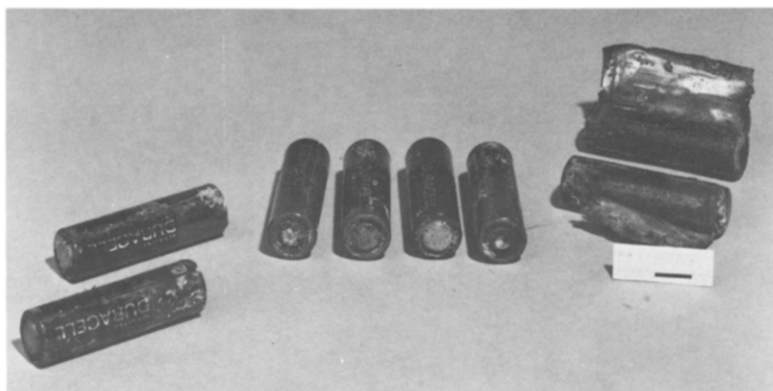
Fig. 13. MN1500 alkaline—manganese batteries. All were fully charged initially. The outer casing was removed from the two right hand batteries to reveal the intact internal steel cases.
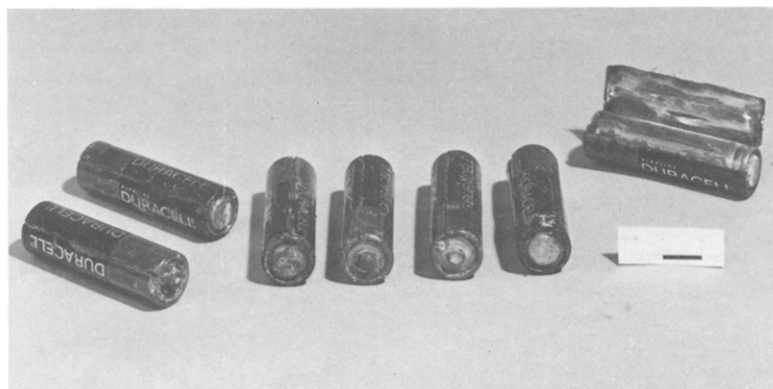
Fig. 14. MN1500 alkaline—manganese batteries. All were discharged before burial. The outer casing was removed from the right hand battery to reveal the inner steel case.


Fig. 15. MN1500 alkaline—manganese batteries. For comparison the top row were charged and the bottom row discharged when buried. The negative terminal buttons (left) were largel largely unattacked while the positive terminal buttons of the charged batteries (top left) were substantially attacked.
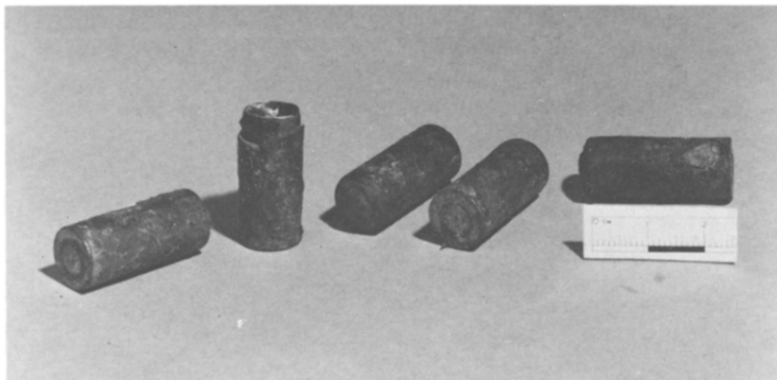
Fig. 16. RM401 mercury batteries. The left hand cell was charged and the others discharged when buried. The second cell from the left was damaged during the excavation.

Fig. 17. RM401 mercury batteries. A close up of the discharged batteries showing the positive and negative terminal buttons and perforation of the battery casing.
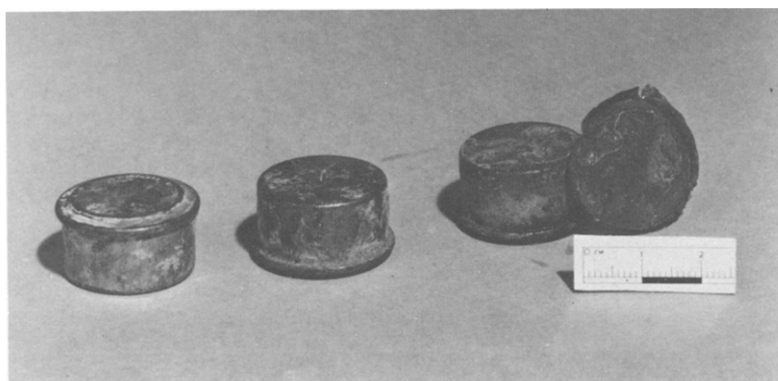
Fig. 18. 400DK nickel—cadmium batteries. All were discharged when buried. The right hand battery shows the corrosion of the positive terminal 'cover plate'.
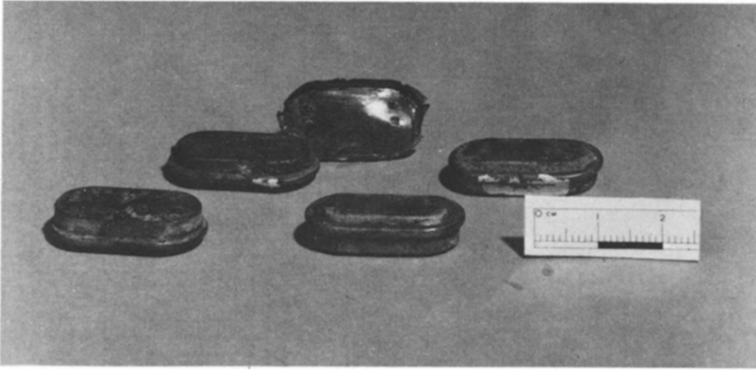
Fig. 19. 90DKO nickel—cadmium batteries. All were charged when buried. The top left hand battery shows the positive terminal 'cover plate' pulled away.
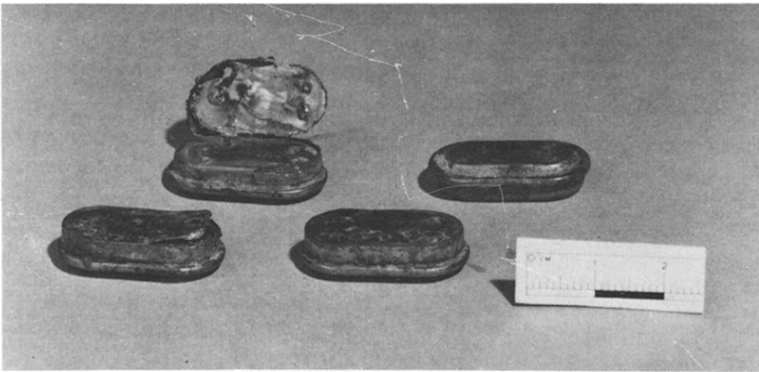

Fig. 20. 90DKO nickel—cadmium batteries. All were discharged when buried. The top left hand battery shows the positive terminal 'cover plate' pulled away.

Fig. 21. SP2 zinc—carbon batteries. Discharged when buried.

Fig. 22. HP7 zinc—carbon batteries. All were charged when buried. Most have the outer plastic wrapper removed to reveal corrosion of the zinc cans.
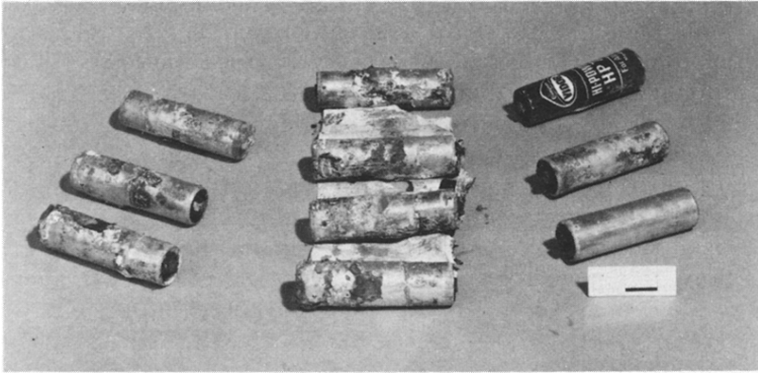

Fig. 23. HP7 zinc—carbon batteries. All were discharged when buried. The outer plastic wrappers of most batteries have been removed to reveal corrosion of the zinc cans.

Fig. 24. HP7 Zinc—carbon batteries. For comparison the left hand batteries were charged and the right hand batteries discharged when buried. The white 'furry' deposits formed on standing in the laboratory.