DISPOSAL CHARACTERISTICS OF SELECTED MILITARY BATTERIES

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Safety Office

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Considerable work has been done to assess the disposal characteristics of CECOM procured military batteries under current U.S. Environmental Protection Agency hazardous waste identification regulations, and State bioassay requirements. This paper presents test results for alkaline, carbon-zinc, magnesium, lithium-manganese dioxide, lithium-sulfur dioxide, and lithium-thionyl chloride batteries. Present findings indicate that: (1) lithium-thionyl chloride and magnesium batteries with greater than 50 percent remaining charge exceed the federal regulatory limit of 5.0 mg/L for chromium, (2) alkaline, carbon-zinc, lithium-manganese dioxide, and lithium-thionyl chloride batteries fail California bioassay toxicity requirements with 96-h LC50 of less than 500 mg/L. Assay methods, findings, disposal requirements, and design implications are discussed.

Military batteries; alkaline, magnesium, lithium batteries; toxic characteristic leaching procedure; bioassay; hazardous wastes; Resource Conservation and Recovery Act (RCRA) regulations

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DISPOSAL CHARACTERISTICS OF SELECTED MILITARY BATTERIES
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Introduction

Over the past ten years considerable work has been done to assess the disposal characteristics of CECOM-procured military batteries using current US Environmental Protection Agency (EPA) hazardous waste (HW) identification regulations, and state bioassay requirements. This paper presents previous and current test methods, results, disposal requirements and design implications for six classes of military batteries procured by the US Army Communications-Electronics Command (CECOM).

We have assessed the disposal characteristics of Army batteries under Resource Conservation and Recovery Act (RCRA) regulations administered by EPA, and state bioassay requirements. This paper presents findings and regulatory management guidance for CECOM-procured alkaline (ALK), zinc-carbon (LCE), magnesium (MG), lithium-manganese dioxide (Li-MnO₂), lithium-sulfur dioxide (Li-SO₂) and lithium-thionyl chloride (Li-SOCl₂) batteries.

Background

RCRA regulations define HW either by listing specific waste streams, or by the identifying specific characteristics under 40 Code of Federal Regulations (CFR) Part 261 Subpart C. Batteries are not listed; and therefore, in order for them to be identified as HW under RCRA, they must be found to be ignitable (D001), corrosive (D002), reactive (D003) or toxic (D004-D043) in accordance with (IAW) established analytical procedures under this regulation. RCRA toxicity regulations became more severe in 1990, when test Method 1311 was changed from the Extraction Procedure Toxicity (EP Tox) test to the Toxicity Characteristic Leaching Procedure (TCLP). This change means, in many cases, that a higher concentration of a TCLP contaminate may be extracted from the sample, than was the case utilizing the EP Tox methodology. A solid waste is determined to be a HW when the extract concentration under TCLP for a particular contaminate is equal to or greater than the "regulatory level (mg/L)" in "Table 1, Maximum Concentration of Contaminants for the Toxicity Characteristic" of 40 CFR 261.24.

All states must utilize RCRA requirements as a minimum for the determination of HW. In addition to RCRA's TCLP the states of Alaska, California, Minnesota, Rhode Island, and Washington utilize bioassay techniques to determine toxicity for HW identification. Bioassay test utilizes an organism's response to a chemical insult to assay toxicity. The measure of toxicity is inversely proportional to the amount of chemical substance to which the organism is exposed. A typical criteria is the lethal concentration (LC) ≤500 mg/L, which is fatal to 50% of the test organisms, i.e. LC₅₀, during a 96 hour (96-h) test period.

Previous Findings
CECOM has analyzed MG and Li-SO$_2$ military batteries$^{1,2}$ prior to TCLP requirements. MG batteries were found to be non-hazardous solid waste (NHSW). Li-SO$_2$ batteries were found to be ignitable (D001), and reactive (D003) under RCRA. The management recommendation for Li-SO$_2$ batteries suggested that the complete discharge of the battery would eliminate D001 and D003 characteristics, thereby allowing for its disposal as a NHSW. US Army laboratory Command (LABCOM) analysis of Li-SOCl$_2$ military batteries$^3$ yielded results and management recommendations similar to those for Li-SO$_2$ batteries.

**Current Efforts**

When the TCLP methodology replaced EP Tox we undertook a major study$^4$ to evaluate ALK, LCE, MG, Li-MnO$_2$, Li-SO$_2$ and Li-SOCl$_2$ military batteries for the toxicity characteristic under TCLP. The other RCRA characteristic tests for ignitability, corrosivity and reactivity were not affected by this 1990 regulatory change. In addition, we decided to analyze these batteries utilizing California's (CA) bioassay methodology. The methodology and results are shown below under analysis 1.

A finding of analysis 1 below, indicated that MG batteries discharged to 50% capacity should be characterized as toxic HW for Cr (D007) under RCRA. This finding was challenged by a major battery supplier.$^5$ The supplier's findings suggested that the TCLP sensitivity for Cr was dependent on the battery's state of charge. This prompted an additional TCLP study$^6$ to clarify this issue. The methodology and results are shown below under analysis 2.

**Analysis 1**

**Method$^{7,8}$**

A random sample, n=42 (7/type), of ALK, LCE, MG, Li-MnO$_2$, Li-SO$_2$ and Li-SOCl$_2$ military batteries were selected from depot stock. Prior to analysis ALK, LCE, MG Li-MnO2 batteries were discharged to 50% of capacity to simulate field conditions prior to disposal. IAW solid waste management guidance$^{2,3}$ Li-SO$_2$ and Li-SOCl$_2$ batteries should be totally discharged prior to disposal; therefore, these batteries were totally discharged prior to analysis.

**TCLP:** The battery samples were then reduced to <9.5mm particle size, and 100g aliquots were extracted IAW TCLP methodology. The extracted leachates were analyzed for metals, volatile organic compounds and semi-volatile organic compounds, except for pesticides and herbicides, IAW SW-846$^9$ as required by Method 1311. Metal leachate samples were analyzed using atomic absorption spectrometry or inductively coupled plasm technique. Volatile organic compounds and semi-volatile organic compounds were analyzed using gas chromatography/mass spectrometry or high performance liquid chromatography as appropriate.

**Bioassay:** Aquatic bioassays were conducted to further characterize HW. CA's
Table 1
Summary of TCLP Results by Battery Chemical Type
n=42\(^1\). Mean (mg/L)

<table>
<thead>
<tr>
<th>TCLP Contaminant</th>
<th>ALK</th>
<th>LCE</th>
<th>MG</th>
<th>Li-MnO(_2)</th>
<th>Li-SO(_2)</th>
<th>Li-SOCl(_2)</th>
<th>TCLP Regulatory Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>0.53</td>
<td>0.190</td>
<td>0.15</td>
<td>0.062</td>
<td>&lt;0.050</td>
<td>0.10</td>
<td>5.0</td>
</tr>
<tr>
<td>Barium</td>
<td>&lt;0.10</td>
<td>0.18</td>
<td>0.88</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>0.15</td>
<td>100.0</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt;0.0030</td>
<td>0.052</td>
<td>0.0033</td>
<td>&lt;0.0030</td>
<td>0.017</td>
<td>&lt;0.0030</td>
<td>1.0</td>
</tr>
<tr>
<td>Chromium</td>
<td>&lt;0.010</td>
<td>0.010</td>
<td>9.1(^2)</td>
<td>0.012</td>
<td>&lt;0.010</td>
<td>4.2(^3)</td>
<td>5.0</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt;0.050</td>
<td>0.186</td>
<td>&lt;0.050</td>
<td>&lt;0.050</td>
<td>&lt;0.050</td>
<td>&lt;0.050</td>
<td>5.0</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.033</td>
<td>0.040</td>
<td>N/A(^4)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>0.2</td>
</tr>
<tr>
<td>Selenium</td>
<td>&lt;0.050</td>
<td>0.058</td>
<td>0.088</td>
<td>&lt;0.050</td>
<td>&lt;0.050</td>
<td>0.082</td>
<td>1.0</td>
</tr>
<tr>
<td>Silver</td>
<td>&lt;0.010</td>
<td>0.036</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Notes: 1. Sub-sample, n=7, for each battery chemistry type.
2. Mean value exceeds regulatory limit.
3. Upper 95% confidence limit around mean exceeded regulatory limit.
4. Lithium and Magnesium batteries do not contain mercury.

Methodology was selected as a representative test.\(^8\) The TCLP method uses an acetate buffer, which is toxic to some aquatic biota. In order to eliminate this confounding variable, Method 1312 from SW-846 was utilized for extraction, which is not toxic to the Fathead minnow and Ceriodaphnia, utilized in CA's methodology. The organisms utilized represent vertebrate and invertebrate species, respectively. Preliminary 48-h \(LC_{50}\) acute toxicity tests were conducted to establish dilution ranges. Acute 96-h \(LC_{50}\) toxicity tests were conducted. The \(LC_{50}\) concentrations (mg of battery/L) reported will kill 50% of the test animals in the specified time period.

Results

TCLP: No volatile organic compounds nor semi-volatile organic compounds were found that exceeded the regulatory limits (RL) established by 40 CFR 261 criteria. The results for "EPA Contaminant" metals are found in Table 1. Fifty percent capacity MG batteries exceeded the 5.0 mg/L RL for Cr. The upper 95% confidence limit around the mean for totally discharged Li-SOCl\(_2\) batteries exceeds the 5.0 mg/L RL for Cr. Under EPA's interpretation Li-SOCl\(_2\) failed the TCLP RL. Therefore, 50% capacity MG batteries, and totally discharged Li-SOCl\(_2\) batteries are considered HW.

Bioassay: Table 2 summarizes the 96-h \(LC_{50}\) acute toxicity results for MG, Li-SO\(_2\), Li-MnO\(_2\), and ALK batteries. \(LC_{50}\) of \(<500\)
mg/L are identified as HW. Preliminary 48-h acute LC$_{50}$ toxicity tests for LCE (LC$_{50}$=289 mg/L) and Li-SOCl$_2$ (LC$_{50}$=2.5 mg/L) batteries identified them as HW under this criteria. 96-h LC$_{50}$ testing for these later two classes of batteries was not required. Li-MnO$_2$, ALK, LCE and Li-SOCl$_2$ batteries are HW under this bioassay criteria.

Table 2

<table>
<thead>
<tr>
<th>Battery Type</th>
<th>Test Organism</th>
<th>Fathead Ceriodaphnia Minnow</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG</td>
<td>22,928</td>
<td>18,067</td>
</tr>
<tr>
<td>Li-SO$_2$</td>
<td>691</td>
<td>702</td>
</tr>
<tr>
<td>Li-MnO$_2$</td>
<td>288</td>
<td>73</td>
</tr>
<tr>
<td>ALK</td>
<td>246</td>
<td>51</td>
</tr>
</tbody>
</table>

Analysis 2

Method

A random sample, n=20 (5/condition), of military MG batteries were selected from independent government test samples previously obtained. Prior to analysis the samples were assigned and pre-conditioned to four state of capacity conditions: 100% (un-discharged), 50% (50% capacity), 10% (10% capacity), and 0% (totally discharged).

TCLP: The samples were prepared and analyzed IAW procedures described under Analysis 1, above.

Results: MG batteries discharged to ≤50% capacity did not exceed RCRA RL for Cr, see Figure 1. No other metals, volatile organic compounds, nor semi-volatile organic compounds exceeded the RLs established by 40 CFR 261 criteria.

Chromium (mg/L)

Figure 1. TCLP Analysis of MG Batteries

Discussion

Methods

The EP Tox method uses a structural integrity test (SIT) to determine the particle size prior to extraction. During previous analysis many battery cells survived the SIT intact, and internal battery/cell structures could not be extracted prior to analysis. This model is inadequate as eventually batteries/cells lose integrity in a landfill disposal site. The TCLP does not utilize a SIT. TCLP requires all components to be "crushed, cut, or ground", such that, the sample particles will pass through 9.5mm sieve prior to extraction and analysis. Solids and liquids are amenable to extraction as well as volatiles in a "zero-headspace extractor" utilized by this method.

There is a great difference between EPA's TCLP and bioassay tests to identify HW. Bioassay is independent for the chemical
compound(s) present. TCLP looks for a particular concentration (mg/L) level of a specific element or chemical compound present, which is defined as a HW. Bioassay is only concerned, if the test animal dies at the LC\textsubscript{50} \leq 500 mg/L. These methods provide two different means of assessing toxicity. It is quite possible that more states may adopt bioassay in the future, particularly those with fragile and extensive wetlands.

Findings

Our findings support the manufacturer’s data, which indicate that available chromium is affected by the battery’s state of charge.\textsuperscript{3} It appears that MG batteries with \textless 50% charge do not exhibit Cr in excess of the RCRA RLs. Management guidance has been provided to user activities, so that, users may test battery capacity prior to disposal.

Environmental Regulations

The characterization of HW for disposal depends on your location and its applicable regulations. Findings aside, we must deal with "NIMBY", that is the Not In My Back Yard syndrome. I can only suggest that it must be dealt with on a case-by-case basis. It is important to get to know your regulator. Even if findings indicate that the material for disposal is a NHSW, the county officials may not allow the waste at the landfill site without a special permit. And with regard to permits, the disposal site’s permit must include your waste stream, or your organization may not use the site.

Waste minimization is another important concept. We have recently commented regarding Docket # F-93-SCSP-FFFFF\textsuperscript{10}, which affects the recycling and reclamation of batteries. Presently New Jersey’s code requires battery recycling. It is important that industry continues to take positive steps to ensure a means to recycle and market spent batteries/cells to reduce the HW stream.

Design

We have already incorporated a complete discharge device in military procured Li-SO\textsubscript{2} and Li-SOCl\textsubscript{2} batteries to eliminate their reactivity prior to disposal. Since MG batteries with \textless 50% capacity are not HW under RCRA, we may consider the same approach in the future for the MG batteries.

Conclusion

The challenge for the future is to identify, isolate, and properly manage hazardous waste to prevent its entering the waste stream. We should and must minimize waste in order to protect our environment and that of our children. This is called pollution prevention, which is the thrust of the Pollution Prevention Act of 1990. We should strive to reduce the waste at its inception, that is by designing our commodities for reuse, remanufacture or recycling. We should attempt to use less hazardous components. We have reduced the mercury content in LCE and ALK batteries. Maybe we can reduce chromium in MG batteries, or increase the life or cycles of secondary batteries. This will help meet the requirements of Executive Order 12856. Only your innovation can achieve these
aids.

References


