Storage Reliability of Reserve Batteries

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Abstract	
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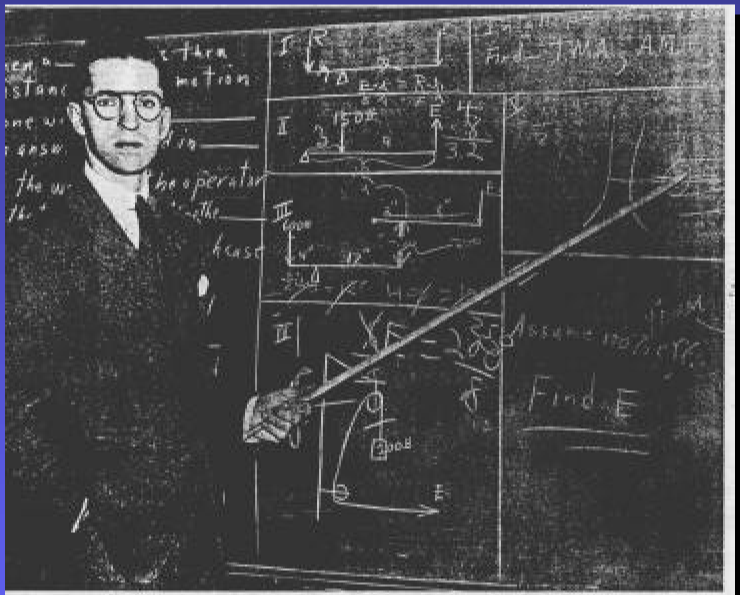
At Issue

- Items developed for munitions have a 20-year shelf life requirement over a wide temperature range
- Developers need to “prove” storage reliability
  - Actual documentation preferred
- Science can be difficult, time-consuming, and costly



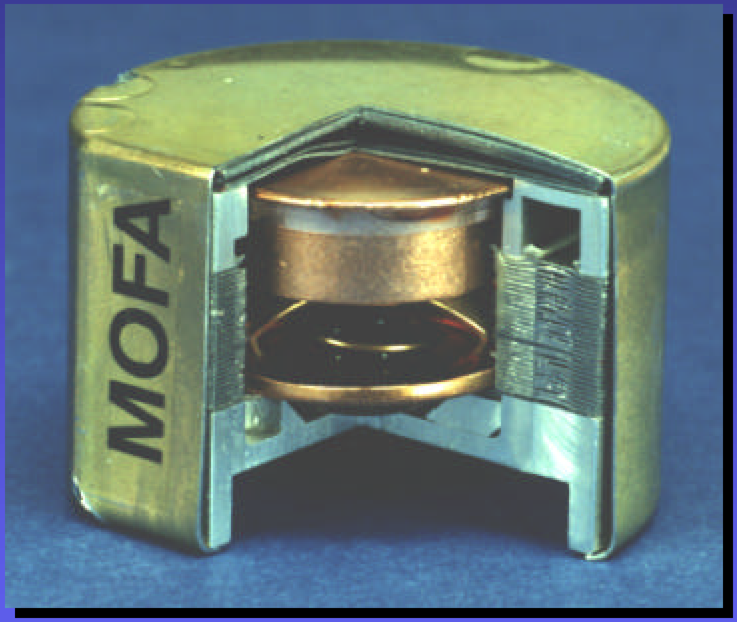
Never mind how we're doing it.

Reservoir Evolution

- Army and Navy used $Pb/HBF_4/PbO_2$ reserve batteries with glass reservoirs
- Over time it was discovered that batteries became more sensitive to activation when dropped
- Glass was being attacked by the aqueous electrolyte
- Drove change to copper dash-pot design

Reservoir Evolution

PS112 Ampoule



ARL MOFA battery (sectioned)

A Common Approach

- Put samples in high-temperature storage
  – Rule-of-Thumb: reaction rates double with every 10°C increase
    - 1 year at 65°C = 16 years at 25°C
- Periodically pull samples and test battery performance
- Analytical work kept to a minimum

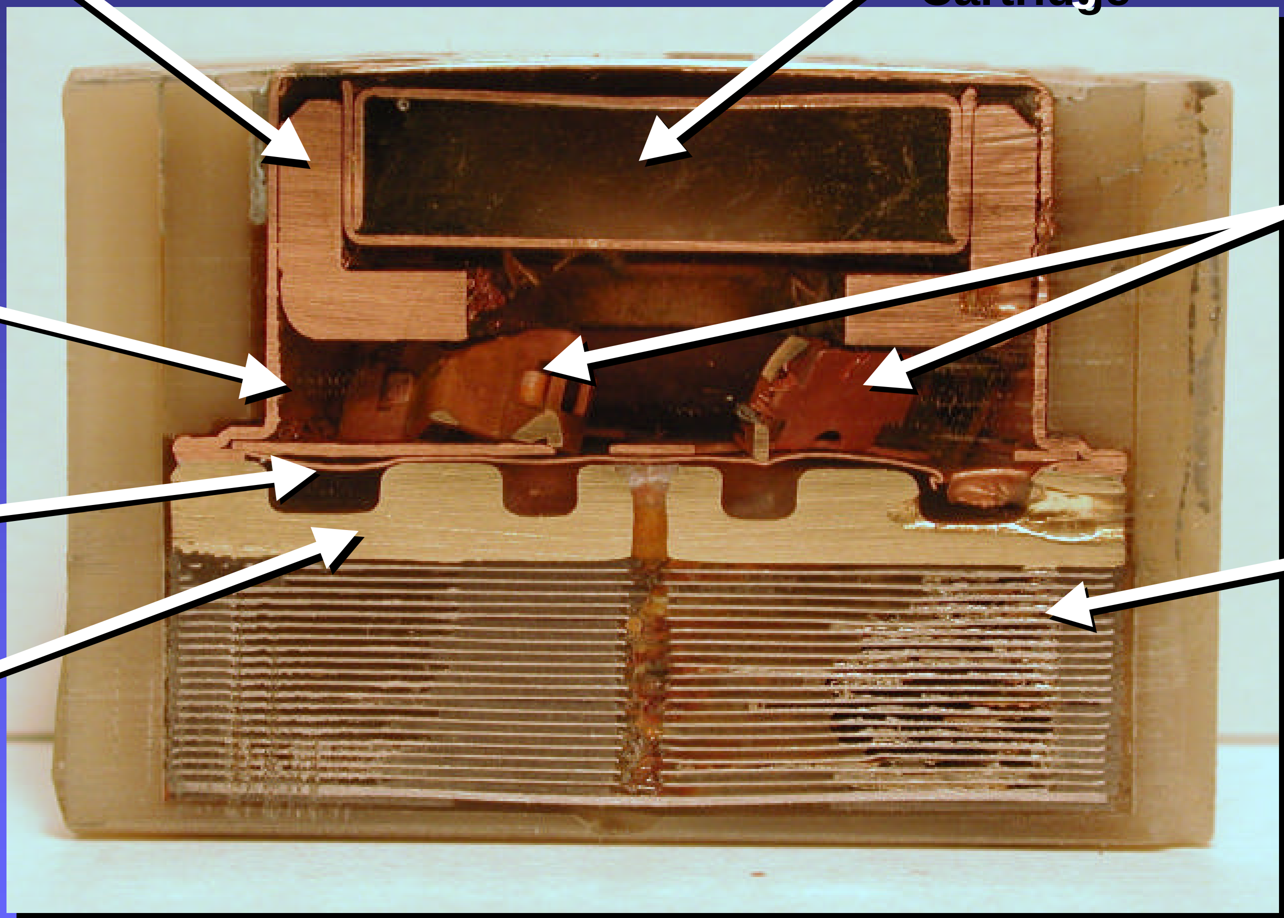
Potential Drawbacks

- Previous slide predicts aging at *25°C*
- How to accelerate aging at high temp conditions?
  - Increase beyond 74°C (165°F), but risk introducing new effects or reactions
  - Increase study time
- Might miss subtle changes that indicate trouble
- Might mask problem altogether

PS115: A Case Study

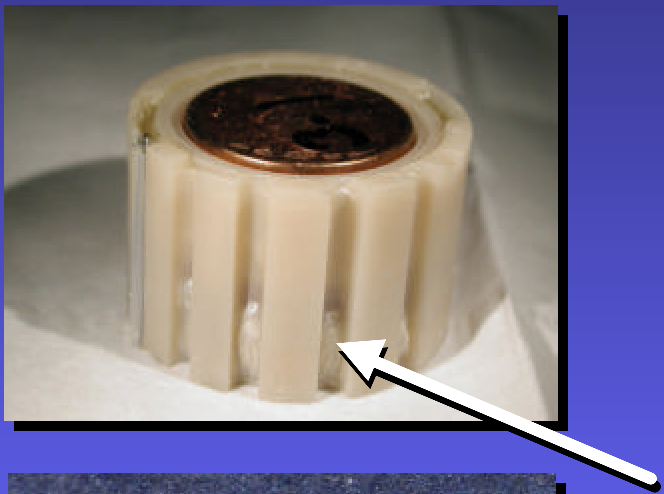
- Dual-fluid, copper reservoir design
  - Fluoboric acid electrolyte
  - Methylene bromide (non-conductive, more dense)
  - Sequenced release of fluids
- Developed in 1964, used in M732 fuze starting in 1978
- Initial studies of reservoir/electrolyte materials indicated they were compatible
- Accelerated aging at 71°C (160°F) indicated no problem

PS115 Section



PS115: Problems Detected

- Production began in 1978
- Five years later, leakage was noticed in engineering samples at HDL
- Further investigation revealed that virtually every lot produced prior to Nov 1980 contained leaking batteries

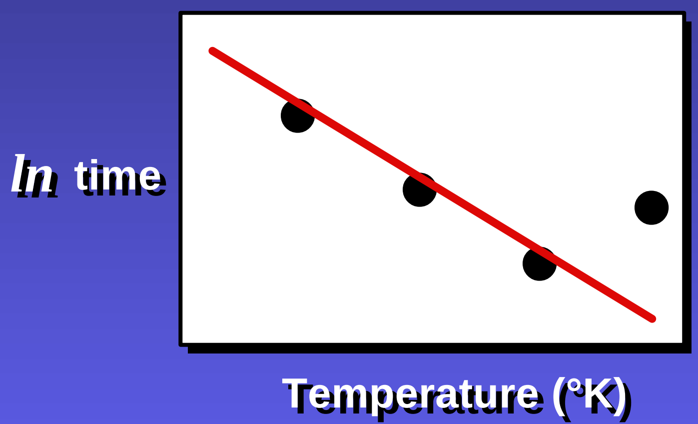


PS115: Investigation Results

- Leakage started earlier and affected a larger percentage of units as temperature increased up to about 60°C (140°F)
- Beyond 60°C, incidents of leakage decreased sharply, essentially reaching zero at about 71°C (160°F)
- Methylene bromide fueled a complex series of reactions with the other reservoir materials
- Above 71°C, increased solubility of copper salts prevented the unique circumstances that caused pitting corrosion and leakage
- High-temp bake-out of reservoir was initial "cure"

A Better Approach

- Store at at least three temperatures
  - determine reaction rates
  - detect changes in behavior
- Use analytical chemistry and optical techniques to measure physical changes
- Determine what is happening, and how fast



Change in Chemistry

- Lead is pretty much history in munitions batteries
  - Environmental concerns, lack of business
  - Non-availability of some critical materials
- Lithium Oxyhalides are systems of choice
  - Good history with single-cell, glass reservoir (barrier munitions, M762 time fuze)
  - Starting to see metal reservoirs in artillery applications (MOFA)
  - Missiles use metal reservoirs
    - 10-year shelf life?
    - Treated better?

Concerns with Oxyhalide Electrolytes

- Very few materials are compatible
- *Extremely* moisture sensitive
  - Reaction products include HCl, SO_2, Cl_2, H_2SO_4
- Some additives/constituents can cause problems
- Can also be affected by light and heat
- Issues have been raised on several current programs
  - Solid forming in electrolyte?

From the Literature

- *Generally speaking*, several metals exhibit good corrosion resistance to neutral electrolytes ($LiAlCl_4$ in thionyl chloride and sulfuryl chloride)
- Using $AlCl_3$ creates a much more corrosive environment (acid electrolyte)
- Of concern in metal containers:
  - heat-treated (welded) areas
  - stressed areas
  - crevice regions
  - metal couples

Some Lessons

- General information is nice, but best to evaluate specific designs
- Great care is required to collect and prepare samples for analysis
- Electrolyte additives should be thoroughly studied prior to implementation

Recommendations

- Start thorough compatibility studies as early as possible, using representative hardware
- Assume studies will take some time and careful planning and execution; quick results likely to be bad news
- Need to understand potential failure mechanism(s): PS115

ARL's Contribution

- Retain in-house Government expertise
- Support contractor's development efforts
- Conduct complementary testing and analysis
- Work to ensure the product meets the Government's requirements
  - Need to independently assess the proposed technology
  - Government needs to be an educated buyer