TESTING, DISSECTION AND ANALYSIS OF LEAD-ACID BATTERIES

Vernon L. Hammersley, and Kevin L. Holloway
Naval Surface Warfare Center, Crane, IN 47522

ABSTRACT

Eight lead-acid batteries were dissected and samples of the electrolyte, negative plate material and positive plate material were subjected to chemical analysis. The results were examined for trends with respect to age.

Introduction

The lead acid batteries under investigation were of the flooded electrolyte design. The chemistry of the battery is of the traditional lead calcium battery with sulfuric acid electrolyte. These batteries are used for back up power. The purpose of this study was to determine the quantity of impurities and to see if trends exist with respect to age of the batteries. The trace element data can be examined to see if the levels are such that the operation and condition of these batteries are affected.

The subject batteries consisted of eight cells for a total voltage of 16 volts. Each battery weighed approximately 1450 pounds and had a capacity of 600 amp-hrs at the 6 hour rate. A total of eight batteries were selected for this particular study. After charging and discharging, the batteries were dissected to determine the condition of internal cell components.

Two cells from each battery were chosen for dissection and retrieval of samples for analysis. The two cells were chosen on the basis of voltage at the end of the previous discharge. The "Best" cell was defined as that cell having the highest voltage and the "Worst" cell was defined as that cell having the lowest voltage.

The electrolyte, positive plate material, and negative plate material were examined chemically in the laboratory. The sulfuric acid electrolyte was analyzed in accordance with the specification¹ and trace elements were determined by inductively coupled plasma spectroscopy (ICP). The positive and negative plate materials were dissolved in acid and analyzed for trace elements by ICP.

Electrolyte Analysis

Most of the tests called for in the specification were conducted on the electrolyte samples. Two different samples of electrolyte were taken from each cell. One sample was taken from the top of the cell while the other sample was poured from the cell. The electrode stack is so tightly configured within the

cell that sampling of electrolyte at various depths was not possible. The two different electrolyte samples allowed for a check of percent sulfuric acid within each cell. Trace element analysis of the electrolyte by ICP allowed a look at possible trends in element concentration within each cell and between cells in the battery as well as between the different batteries.

Tabulated below are the specific gravity and percent sulfuric acid data for the different age groups. When comparing the two cells from the same battery, the worst cell contained slightly lower sulfuric acid content. The sample from the top of the cell, which is unmixed, also contained a lower amount of sulfuric acid when compared to the mixed sample. However, the batteries had not received a boost charge for up to six months prior to dissection, which may have contributed to this slight variation in specific gravity reading. The 19 year old and 23 year old batteries designated as number one in the electrolyte data in Table I were of marginal capacity.

Table I. Sulfuric Acid Electrolyte Data

Age	Cell Cond.	Cell Pos.	Spec. Grav.	%H ₂ SO ₄
5	Best	Top	1.215	28.59
5	Best	Mixed	1.216	28.69
5	Worst	Top	1.213	28.62
5	Worst	Mixed	1.215	28.74
10	Best	Top	1.230	30.82
10	Best	Mixed	1.234	30.95
10	Worst	Top	1.220	29.19
10	Worst	Mixed	1.222	29.49
16	Best	Top	1.192	26.16
16	Best	Mixed	1.222	29.86
16	Worst	Top	1.190	26.25
16	Worst	Mixed	1.219	29.47
19#1	Best	Mixed	1.198	27.30
19#1	Best	Top	1.194	26.42
19#1	Worst	Top	1.191	25.97
19#1	Worst	Mixed	1.198	26.92
19#2	Best	Top	1.213	28.81
19#2	Best	Mixed	1.220	29.65
19#2	Worst	Top	1.205	27.68
19#2	Worst	Mixed	1.206	28.23
21	Best	Top	1.191	26.10
21	Best	Mixed	1.197	26.79
21	Worst	Top	1.180	24.76
21	Worst	Mixed	1.191	26.46
23#1	Best	Mixed	1.207	27.92
23#1	Best	Top	1.165	22.62

23#1	Worst	Mixed	1.192	25.83
23#1	Worst	Top	1.170	22.95
23#2	Best	Mixed	NP	29.35
23#2	Worst	Mixed	NP	30.03
SPECS			1.210-1.220	28.4-29.6

LETTER DESIGNATION IS AS FOLLOWS: NP=NOT PERFORMED

The electrolyte was analyzed by ICP and the results of the mixed sample from one cell are shown in Table II below. These results are typical of the other cell sample that were analyzed.

Table II. ICP Data for Sulfuric Acid

Element/cell	Battery Serial Numbers							
	5	10	16	19#1	19#2	21	23#1	23#2
copper	0	0	0	0	0	0	tr	0
iron	9.6	8.0	12	17	13	17	33	7.9
manganese	0	0	0	0	0	0	tr	0
nickel	tr	0	0	tr	0	0	tr	0
magnesium	112	125	34	23	28	24	64	25
zinc	3.6	4.0	1.7	8.3	2.2	7.2	35	7.7
calcium	203	163	160	98	113	102	283	NP

tr=trace (<1 ppm), NP=not performed

These impurities can affect gassing rate, cause deterioration of separators, increase buildup of lead sulfate in the plates, or change the polarization of the plates². No trends in trace metal quantities were noted with respect to age of these batteries. The long life and maintenance history of these batteries leads to the conclusion that the impurity levels are not affecting their operation in these ways³.

Negative Plate Sample Preparation

For ICP analysis the maximum amount of sample in the smallest volume is desirable. This allows lower detection limits, a stronger signal, greater signal to noise ratio and more accurate as well as precise results. The negative plate material from a charged lead-acid battery consists of lead. Lead sulfate will be present if some discharging and sulfation has taken place. Although the handbooks and other literature identify acids for dissolution of these materials it was found that the simple use of the recommended acids was not successful. Problems with conversion of the lead into either lead chloride or lead nitrate were encountered. These salts are less soluble in concentrated acids than in water. Even though the trace metals may be in solution the presence of a white precipitate in the volumetric flask during the early stages of this project always presented the threat of clogging the capillary tubing used by the ICP to aspirate the sample liquid into the plasma. When a precipitate is present there is also the possibility of occlusion of compounds of other elements within that precipitate. Starting sample size and final volume after boiling were very critical for insuring the dissolution of the resultant precipitate after cooling and diluting. The dissolution procedure which proved successful is as follows: Weigh 0.2 gram of negative plate

material into a 150 ml beaker. Add 40 mls of aqua regia (3HCl:1HNO₃) and boil on a hot plate. Allow volume to reduce until precipitation begins. Remove from hot plate, cool, add 20 mls of aqua regia and return to hot plate. Allow volume to reduce to about 25 mls. Cool. The precipitate is lead chloride. Add water and transfer to 100 ml volumetric flask. Swirl to dissolve precipitate and bring to mark with water. This sample solution is run straight on the ICP. Appropriate dilutions are required if certain elements exceed the most concentrated standard.

ICP Analysis of Negative Plates

Two different sections of the plate were taken for material analysis. One sample was taken from the center and the other sample was taken from the lower left section of the plate. Calcium, iron, magnesium and zinc were detected in all eight batteries. Additionally, a trace of manganese was detected in the second 23 year old battery. A trend in calcium quantity was noted in all batteries. The lower left sample contained significantly more calcium than the center sample. No trends were noted for the other elements detected. Typical data are included in Table III below.

Table III. ICP Data for Negative Plates

Element ppm	Battery Serial Numbers							
	5	10	16	19#1	19#2	21	23#1	23#2
Ca								
Best	122C	122C	57.1C	55.0C	51.3C	79.4C	154C	184C
	251L	238L	260L	303L	167L	228L	181L	158L
Worst	142C	102C	66.1C	82.5C	55.4C	62.7C	192C	91.2C
	198L	180L	270L	218L	218L	171L	219L	187L
Fe								
Best	48.9	54.1	48.6	30.1	57.2	90.8	61.8	27.0
Worst	54.1	43.1	49.2	28.9	57.9	88.6	49.7	31.9
Mg								
Best	21.3	29.2	3.59	5.54	4.80	4.09	22.6	24.3
Worst	28.9	28.2	4.79	4.97	5.82	5.13	11.1	16.7
Zn								
Best	24.5	26.2	8.38	7.90	33.4	20.4	33.5	18.2
Worst	22.8	23.8	15.3	8.21	23.0	19.1	35.5	12.7

C=CENTER OF PLATE, L=LOWER LEFT OF PLATE

Positive Plate Sample Preparation

The positive plate material in a charged lead-acid battery consists of lead dioxide. Lead sulfate, the discharged product, may also be present. Dissolution of this material was attempted by trying various ratios of nitric acid and hydrogen peroxide. The conversion of the lead species into lead nitrate proved to be troublesome. As mentioned before lead nitrate is only sparingly soluble in nitric acid. The more

concentrated the acid the less soluble the nitrate. Initially, 30% hydrogen peroxide was used in mixture with nitric acid. In this case more is not better. The final concentration of hydrogen peroxide was considerably less. An analytical text⁴ which covered the analysis of lead dioxide revealed this. The appropriate procedure for complete dissolution of a one gram sample of positive plate material was as follows: Weigh one gram of positive plate material into a 150 ml beaker. Add 15 mls of previously boiled concentrated nitric acid, 10 mls of 1% hydrogen peroxide and 50 mls of hot water. Heat on a hot plate until dissolution is complete. Transfer to a 100 ml volumetric flask and dilute to the mark with water. This sample solution is run straight on the ICP. Appropriate dilutions are required if certain elements exceed the most concentrated standard.

ICP Analysis of Positive Plates

Calcium, iron, magnesium and a trace of manganese were detected in all eight batteries. A trend in calcium quantity was noted in all batteries except the second 23 year old battery. The trend consisted of larger quantities of calcium in the lower left sample than in the center sample. No trends were noted for the other elements detected. Typical data are shown in Table IV below.

Table IV. ICP Data for Positive Plates.

Element ppm	Battery Serial Numbers							
	5	10	16	19#1	19#2	21	23#1	23#2
Ca								
Best	18.3C	12.8C	54.1C	15.5C	13.7C	27.0C	31.3C	29.2C
	97.7L	88.3L	167L	131L	89.6L	115L	104L	44.6L
Worst	48.7C	18.3C	73.6C	22.0C	15.7C	29.4C	53.2C	19.5C
	103L	19.1L	132L	130L	95.3L	94.9L	58.6L	60.4L
Fe								
Best	23.6	24.9	35.5	36.5	36.0	100	69.5	49.8
Worst	21.6	28.6	31.8	36.8	45.0	50.3	62.0	31.5
Mg								
Best	18.6	20.8	3.73	4.48	3.66	6.01	11.7	2.32
Worst	15.8	25.1	3.46	4.64	4.11	3.74	12.3	2.27
Mn								
Best	tr	0	0	tr	tr	tr	tr	tr
Worst	tr	0	0	tr	tr	tr	tr	tr
Zn								
Best	0	0	2.17	0	8.33	20.0	0	0
Worst	0	0	1.99	0	8.07	12.5	0	0

C=CENTER OF PLATE, L=LOWER LEFT OF PLATE, tr=trace (<1 ppm)

Spectroscopic Considerations

Instruments such as an emission spectrograph or inductively coupled plasma (ICP) spectrometer are powerful tools for chemical analysis. However, the closeness of emission lines of two different elements to one another can cause problems,

especially when quantitative analysis is being conducted. This was noted when analyzing a sample of sulfuric acid electrolyte on a later job with the ICP. Initially, it appeared the sample contained a large amount of platinum. Manufacturer's specs indicated platinum should not be present. Analysis also detected cadmium. An examination of the MIT Wavelength Tables showed the platinum analytical line used by the instrument was only 0.15 Angstroms below a strong cadmium line. The following lines were noted from the table: Platinum 2144.231 Angstroms, NIST intensity units 1900, Cadmium 2144.382 Angstroms, NIST intensity units 19,000. If 200 ppm of cadmium were present the instrument could record it as 2000 ppm of platinum. Cadmium was determined on this sample by using a wavelength far removed from the platinum analytical line.

The specification for the subject electrolyte samples did not call for cadmium determination. When platinum was apparently detected its presence was checked with a qualitative test from the specification¹. The qualitative test was sensitive to 20 ppm of platinum and none was detected in the suspect electrolyte samples. As little as 1 ppm platinum in the negative plates can cause violent gassing, resulting in partial removal of negative plate material². No such problem was observed in these batteries.

Conclusions

Trends in calcium levels with respect to age were noted in the negative and positive plates. The two 23 year old batteries had calcium levels distributed evenly between the center and lower left areas of the plate. The batteries with fewer years of age showed more calcium in the lower left area of the plate. No trends in trace metal quantities were noted with respect to age of these batteries. The long life and maintenance history of these batteries leads to the conclusion that the impurity levels are not affecting their operation.³ Trace element levels are not such that battery life would be affected.

References

1. Federal Specification O-S-801C, Amendment 2.
2. A General Treatise on the Physics & Chemistry of Secondary Batteries & their Engineering Applications by George Wood Vinal, 4th edition, 1955, John Wiley & Sons.
3. RN-145 Flooded Lead Acid Battery Aging and Surveillance Report and Service Life Estimate, 1 June 1995 by V.J. Ang and F.A. Oley.
4. Scott's Standard Methods of Analysis by N.H. Furman, editor, 6th edition, D. Van Nostrand Company, Inc., pages 577-578.