

INTERNATIONAL LEAD ZINC RESEARCH ORGANIZATION, INC.

1. PLAN WORK
2. REPORT
3. REPORT
4. REPORT
5. REPORT
6. REPORT
7. REPORT
8. REPORT
9. REPORT
10. REPORT
11. REPORT
12. REPORT
13. REPORT
14. REPORT
15. REPORT
16. REPORT
17. REPORT
18. REPORT
19. REPORT
20. REPORT
21. REPORT
22. REPORT
23. REPORT
24. REPORT
25. REPORT
26. REPORT
27. REPORT
28. REPORT
29. REPORT
30. REPORT
31. REPORT
32. REPORT
33. REPORT
34. REPORT
35. REPORT
36. REPORT
37. REPORT
38. REPORT
39. REPORT
40. REPORT
41. REPORT
42. REPORT
43. REPORT
44. REPORT
45. REPORT
46. REPORT
47. REPORT
48. REPORT
49. REPORT
50. REPORT
51. REPORT
52. REPORT
53. REPORT
54. REPORT
55. REPORT
56. REPORT
57. REPORT
58. REPORT
59. REPORT
60. REPORT
61. REPORT
62. REPORT
63. REPORT
64. REPORT
65. REPORT
66. REPORT
67. REPORT
68. REPORT
69. REPORT
70. REPORT
71. REPORT
72. REPORT
73. REPORT
74. REPORT
75. REPORT
76. REPORT
77. REPORT
78. REPORT
79. REPORT
80. REPORT
81. REPORT
82. REPORT
83. REPORT
84. REPORT
85. REPORT
86. REPORT
87. REPORT
88. REPORT
89. REPORT
90. REPORT
91. REPORT
92. REPORT
93. REPORT
94. REPORT
95. REPORT
96. REPORT
97. REPORT
98. REPORT
99. REPORT
100. REPORT

888 MADISON AVENUE, NEW YORK, N. Y. 10017
TELEPHONE 875-8020 (AREA CODE 212)
CABLE ADDRESS NYLZRO NEW YORK

March 7, 1966

To: Chairman, Lead Industry Development Committee
Chairman, Lead Technical Steering Committee
Lead Electrochemical-Metallurgical Subcommittee
Dr. S. P. Radtke

From: A. E. Cook

Subject: LE-99 - Recombination of Gases in Lead Acid Batteries

Attached is a copy of a report on a meeting recently held at the Polytechnic Institute of Brooklyn to initiate the above program. I have made the report unusually detailed since the application of calorimetric techniques to the study of lead acid batteries is quite unusual and I am anxious that all concerned should have the opportunity to be fully conversant with the work. Please note the Appendix to the Report, which is an independent appraisal of the use of calorimetric techniques to problems of this type.

We have been impressed with Brooklyn Polytechnic Institute's approach and look forward to a very successful program.

A. E. Cook

ARC:ms
enclosures

CC: Dr. A. Salkyud
Mr. E. Ritchie
Dr. W. Zeek
Dr. Paul Bruins
Mr. Stanley Coulter

VISIT REPORT

March 3, 1966

Date of Visit: February 21, 1966To: Polytechnic Institute of Brooklyn
333 Jay Street
Brooklyn, New YorkThose Present: Dr. A. Salkynd.....Electric Storage Battery Co.
Mr. E. Ritchie.....Eagle-Picher Company
Dr. W. Zeek.....C. Tennant and Sons
Mr. A. R. Cook.....ILZRO
Dr. Paul Bruins.....Polytechnic Institute of Brooklyn
Mr. Stanley Caulder,
Research Fellow....Polytechnic Institute of BrooklynPurpose: To set up the research program for LE-99 -
"Recombination of Gases in Lead Acid Batteries"
and arrange industry cooperation.Summary: There was unanimous agreement on the course of action
decided. Non-specialists in the battery field may be
interested in the appendix to this report outlining
how calorimetric studies can be applied to the study
of lead acid batteries.Action: Mr. S. Caulder, with guidance from Dr. A. Salkynd and
Prof. Bruins, will commence work on the program as
outlined below.Dr. Zeek will supply copies of the ALDA bibliography
on lead batteries.

A. R. Cook will set up the next meeting for mid-June.

Mr. Ritchie will supply samples as detailed in the
report.Acknowledgments: ILZRO would like to acknowledge the assistance pro-
vided by Dr. W. Zeek, Dr. A. Salkynd and Mr. E.
Ritchie in setting up this program, and to Dr. Zeek
in correcting the draft of this report.

ARC:ms

CC: Dr. S. P. Radtke
Lead Electrochemical-Metallurgical Subcommittee
Chairman, Lead Technical Steering Committee
Chairman, Lead Industry Development Committee

N 3363.01

-2-

The program, as agreed to, can be considered in three parts as follows:

1. Commercial Cell Study:

Initial calorimetric experiments will be conducted with a small commercial lead acid cell, the ES-240. This work will provide an initial idea of the level of the heat effects as background for the later work. In addition, the construction of the cell is such that the sensing thermistors can easily be inserted into it, and pressure measuring devices can be attached. Thus the heat balance can be measured as a function of electrolyte concentration and polarization, and simultaneous measurement can be made of pressure changes.

2. Experimental Cell Study:

A number of miniature electrochemical cells will be constructed for study in a plastic pressure bomb which will in turn be placed in the calorimeter. Pressure will be in the range 1/2 to 5 atmosphere positive pressure. The negative grids to be studied will be made of:

- (a) Pure lead
- (b) Calcium (0.5%) lead alloy
- (c) Antimony (6%) lead alloy
- (d) Dispersion hardened lead.

To avoid antimony contamination of the negatives, the positive plates and grids to be used will be made with 0.5% calcium lead alloy (calcium does not transfer to the

-3-

negative). In the case where pasted negative plates are required, it has been suggested that a certain amount of so-called "expanders" be included. (Expanders are materials which prevent the negative plates from densifying during cycling.) $1/2\%$ Barium Sulphate was discussed as a suitable additive; neither carbon black nor organic additives were regarded as suitable due to the limited number of cycles involved. Attrition mill oxides will be used. Paste density will be in the medium dense range. Reagent grade acid was judged suitable. Both bare negative grids and small pasted plates will be tested against pasted positive plates, and excess positive capacity will always be present. The cell will be charged either at various constant potentials or constant currents, and the heat and pressure effects will be measured as well as the operating potentials and currents. It should be noted that the heats of reaction of some of the reactions which are expected to occur are known, but the exact conditions of onset in a lead acid cell are not, and it is anticipated that these conditions can be determined. For example, the onset of hydrogen evolution cannot be determined easily by visual means, but it should be readily recognised by the heat effects.

Some of the variables which must be considered in this study are:

- (a) Total electrode surface
- (b) The oxygen pressure
- (c) The reference potential on the electrodes

-4-

- (d) Volume of the electrolyte
- (e) Electrolyte concentration
- (f) Electrolyte viscosity
- (g) Rate of charge

Single electrode potentials will be measured using mercury/mercurous sulfate reference electrodes. It has been suggested that the 5, 10 and 20 hour rates be used in charging the cells, and that provision be made for stirring the electrolyte. All plates will be totally immersed in the electrolyte.

3. Charge efficiency of the negatives

It is very important that only oxygen be evolved during charging of a lead acid cell if recombination is to take place and the cell is to be sealed. If hydrogen is evolved it will leak out through the case, and the cell will gradually get out of balance. (A nickel cadmium sealed cell is operated so that no hydrogen is evolved.) In order to insure that the cell is constructed and operated so that no hydrogen is evolved, the efficiency of the negative plate must be known. Since the usual limiting factor in lead acid battery operation is the charge efficiency of the positive plates, very little has been done to measure the charge efficiency of negatives. This is of prime importance in our program and a study of negative efficiency will be made concurrently with the calorimetric studies.

-3-

It was felt that it would be valuable to have the same materials used in this program as are under study at the Naval Research Laboratory. Since these are supplied by the Eagle-Picher Company, Mr. Everett Ritchie kindly agreed to furnish the grids and alloys for this program. He will furnish the following:

<u>Metal</u>	<u>Bare Grids</u>		<u>Pasted Plates</u>		<u>Positives</u>	<u>Total</u>
	<u>Negatives</u>	<u>Positives</u>	<u>Negatives</u>			
			<u>Inorganic Expander</u>	<u>Organic Expander</u>		
Soft Pb	8	0	8	8	0	24
6% Sn	8	0	8	8	0	24
Cu-Pb	8	64	8	0	96	176
18-Pb	8	0	8	0	0	16

It was also agreed that Eagle-Picher would assist by the lead plating terminals to provide necessary corrosion protection.

Note:

A section on electrochemical calorimetry taken from the Encyclopedia of Electrochemistry is attached to provide a further background for this calorimetric study.