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ANALYSIS FOR NICKEL (III AND IV) IN POSITIVE PLATES FROM NICKEL-CADMIUM CELLS

INTRODUCTION

The NASA-Goddard procedure for destructive physical analysis (DPA) of nickel-cadmium cells contains a method for analysis of residual charged nickel as NiOOH in the positive plates at complete cell discharge, also known as nickel precharge. In the method, the Ni(III) is treated with an excess of an Fe(II) reducing agent and then back titrated with permanganate. The Ni(III) content is the difference between Fe(II) equivalents and permanganate equivalents.

Problems have arisen in analysis at NAVSURFWARCENDIV, Crane because for many types of cells, particularly AA-size and some "space-qualified" cells, zero or negative Ni(III) contents are recorded for which the manufacturer claims 3-5% precharge.

Our approach to this problem has been to reexamine the procedure for the source of error, and correct it or develop an alternative method.

EXPERIMENTAL

In this work, results will be presented from analysis of two brands of AA-size cells, 12Ah and 20Ah space qualified cells, and a 30Ah cell from an aircraft battery.

The role of the iron reducing agent was investigated by using the standard reagent, ferrous ammonium sulfate (FAS), ferrous sulfate (FeS), and prepared FAS (FeS + ammonium sulfate (AS)). Also, the possibility of using a substitute reducing agent was investigated with stannous chloride (TDC, tin dichloride).

RESULTS AND DISCUSSION

Table 1 illustrates the problems encountered with the five plate sample materials when FAS is

TABLE 1
Residual NiOOH Content For Five Plate Sample Materials

30Ah Aircraft Battery Cell		G-AA Cell (3 Cells)	
1. 5.75%	2. 5.52%	1. -1.48%	2. -1.70%
3. 4.83%	4. 5.48%	3. -1.20%	4. -1.10%
5. 5.93%	6. 5.18%	5. -1.51%	6. -0.85%

20Ah Space Cell		S-AA Cell (3 Cells)	
1. -0.09%	2. -1.23%	1. -3.76%	2. -2.97%
3. -0.51%	4. -0.31%	3. -1.26%	4. -1.70%
5. -1.30%	6. -0.47%	5. -2.38%	6. -1.67%

12Ah Space Cell	
3. 3.17%	4. 3.26%
1. 3.72%	2. 3.32%

the reductant. A search for an alternative reagent for the reduction step resulted in the selection of TDC. In Table 2 are given the analytical results for FAS and TDC in side-by-side analyses.

TABLE 2
Comparison Of Residual NiOOH Results
For FAS And TDC

Sample Description	%NiOOH
1. 0.1394g GAA Ni + 0.4002g FAS	0.55
2. 0.1392g GAA Ni + 0.4007g FAS	0.64
3. 0.1400g GAA Ni + 0.1106g TDC	2.30
4. 0.1396g GAA Ni + 0.1112g TDC	1.97
5. 0.1390g SAA Ni + 0.3995g FAS	-1.57
6. 0.1398g SAA Ni + 0.4000g FAS	-1.48
7. 0.1400g SAA Ni + 0.1108g TDC	1.41
8. 0.1403g SAA Ni + 0.1107g TDC	1.35
9. 0.1408g 20Ah SC + 0.3987g FAS	-1.02
10. 0.1405g 20Ah SC + 0.3994g FAS	-1.24
11. 0.1388g 20Ah SC + 0.1096g TDC	3.43
12. 0.1412g 20Ah SC + 0.1089g TDC	3.18
13. 0.1420g 12Ah SC + 0.4013g FAS	2.69
14. 0.1403g 12Ah SC + 0.3995g FAS	3.09
15. 0.1393g 12Ah SC + 0.1112g TDC	8.32
16. 0.1414g 12Ah SC + 0.1103g TDC	8.01
17. 0.1389g 30Ah AB + 0.4000g FAS	5.21
18. 0.1399g 30Ah AB + 0.4006g FAS	4.61
19. 0.1412g 30Ah AB + 0.1120g TDC	7.61
20. 0.1400g 30Ah AB + 0.1110g TDC	8.17

The TDC data are uniformly positive, and in the ranges expected for the respective cells.

In the procedure, a magnetic stirbar is used, and at the conclusion of the reduction period, it is removed to prevent the metal particulates which cling to the bar from interfering in the permanganate back titration. The data in Table 3 illustrate the consequences, shown for FAS and TDC, of leaving one of the metal particulates, iron, in the samples during permanganate titration. With FAS, the amount of titrant required increases steadily with increasing iron content, while the TDC titration is practically unaffected by the particulate iron. Normally, the particulates are removed before the titration step, but a different interaction definitely occurs with the sample particulates during the titration step when FAS is the reductant compared to when TDC is used. Similar results are obtained for particulate nickel and cobalt.

TABLE 3
Effect Of Metallic Iron On Expected Titers

Sample Description	Act. MnO_4^-	Theo. MnO_4^-
FAS		
1. 0.4500g	11.55ml	11.48ml
2. 0.4478g	11.40ml	11.43ml
3. 0.4483g + 0.0094g Fe*	11.45ml	11.44ml
4. 0.4496g + 0.0103g Fe*	11.50ml	11.47ml
5. 0.4505g + 0.0109g Fe@	16.00ml	11.48ml
6. 0.4507g + 0.0204g Fe@	20.70ml	11.50ml
7. 0.4500g + 0.0300g Fe@	25.10ml	11.48ml
TDC		
1. 0.1286g	10.90ml	10.92ml
2. 0.1327g	11.30ml	11.27ml
3. 0.1298g + 0.0104g Fe*	11.00ml	11.02ml
4. 0.1297g + 0.0096g Fe*	11.00ml	11.01ml
5. 0.1296g + 0.0103g Fe@	11.00ml	11.00ml
6. 0.1322g + 0.0123g Fe@	11.30ml	11.23ml

* stirbar removed prior to titration
@ stirbar left in during titration

In an attempt to obtain more information about the interaction of reducing agents with the metal particulates prior to the back titration in the analysis, a series of analyses were performed with AB plate materials, with the following reductant combinations: FAS, FeS, FeS + AS, and TDC. In the cases where AB plate material was used, in half the samples with each reductant the stirbar with particulates was removed prior to acidification with H_2SO_4 and titration, while in the other half, the stirbar was left in during the MnO_4^- titration. In Table 4a the results for the Ni(III) titrations are given, while in Table 4b the analyses for the residues are presented. In the residues, only iron and nickel were found present to any extent, and trace amounts of cadmium and cobalt were also noted. Therefore, only the Fe and Ni are reported in Table 4b.

TABLE 4a
AB Nickel Plate Material Analysis With
Several Reducing Agents

Sample Description (wt Ni + wt FeS)	Vol MnO_4^-	% NiOOH
1. 0.1401 + 0.3010	10.82*	7.08
2. 0.1402 + 0.3002	10.80*	7.00
3. 0.1411 + 0.3012	10.85*	6.89
4. 0.1409 + 0.2998	27.25@	----
5. 0.1407 + 0.3008	26.75@	----
6. 0.1301 + 0.3000	28.75@	----

TABLE 4a (cont.)

Sample Description	Vol MnO_4^-	% NiOOH
wt Ni + wt FeS + Wt AS		
7. 0.1399 + 0.3006 + 0.1206	10.85*	6.79
8. 0.1412 + 0.2995 + 0.1202	10.80*	6.77
9. 0.1408 + 0.3006 + 0.1203	10.80*	7.08
10. 0.1407 + 0.2995 + 0.1200	27.15@	----
11. 0.1409 + 0.3008 + 0.1999	28.10@	----
12. 0.1402 + 0.3004 + 0.1202	28.65@	----
wt Ni + wt FAS		
13. 0.1396 + 0.4208	9.80*	6.08
14. 0.1399 + 0.4198	9.90*	5.23
15. 0.1400 + 0.4208	9.85*	5.66
16. 0.1403 + 0.4204	23.95@	----
17. 0.1403 + 0.4196	27.85@	----
18. 0.1405 + 0.4208	27.65@	----
wt Ni + wt TDC		
19. 0.1392 + 0.1270	9.55*	8.60
20. 0.1396 + 0.1282	9.60*	8.92
21. 0.1411 + 0.1277	9.70*	7.89
22. 0.1398 + 0.1292	9.80@	8.15
23. 0.1405 + 0.1277	9.80@	7.28
24. 0.1390 + 0.1278	9.70@	8.07

TABLE 4b
Residue Analysis (wt $\times 10^{-2}$)

Sample	g Res	g Fe	g Ni	Equiv MnO_4
1.	----	0.0146	6.33	21.67
2.	----	0.0161	6.03	20.68
3.	----	0.0169	6.32	21.65
4.	----	0.0087	1.13	3.90
5.	----	0.0103	0.0953	3.31
6.	----	0.0059	0.120	4.09
7.	----	0.0160	6.62	22.67
8.	----	0.0144	6.61	22.63
9.	----	0.0167	6.41	21.96
10.	1.62	0.0100	1.29	4.46
11.	1.62	0.0117	0.82	2.86
12.	1.75	0.0086	0.78	2.71

TABLE 4b (cont.)
Residue Analysis (wt x10^{-2})

Sample	g Res	g Fe	g Ni	Equiv MnO_4^-
13.	7.03	0.0144	5.92	20.27
14.	6.24	0.0183	5.88	20.15
15.	7.27	0.0182	5.78	19.81
16.	2.24	0.0097	1.74	5.98
17.	1.09	0.0082	0.48	1.68
18.	1.30	0.0087	0.69	2.40
19.	7.78	0.0004	5.77	19.69
20.	7.70	0.0006	5.72	19.52
21.	6.43	0.0002	5.28	18.00
22.	7.22	0.0003	5.29	18.04
23.	7.08	0.0006	5.43	18.53
24.	7.20	0.0007	5.31	18.12

The data in Table 4a show that the Fe(II)-based reductants give a consistently lower ß-NiOOH content for the discharged positive plate material than TDC. The average of the sum of sets 1-3, 7-9, and 13-15 is 30% lower than the average of the set 19-21, and the FAS data alone are 50% lower, on average. Thus, there is a clear difference between Fe(II) and Sn(II) reduction. Also, the presence or absence of ammonium ion is not a significant factor in the observations. Finally, it appears that leaving the particulate-clad stirbar in the TDC solutions during MnO_4^- titrations may yield a slightly lower ß-NiOOH content, so that it is advisable to remove it prior to titration.

The data in Table 4b show that the principle component of the particulate matter is, not surprisingly, nickel. However, it also appears that there is considerably more residual iron in the Fe(II)-based solutions than in the TDC solutions, by a factor of 35-40X. If Fe(II) is being reduced to Fe(0) in samples 1-18, what is the reductant? If Fe(0) is being oxidized in samples 19-21 (before MnO_4^- titration), only Ni(III) could be the oxidant, but then less Sn(II) would be oxidized by Ni(III), so the eventual titer with MnO_4^- would be too large, leading to a low value for ß-NiOOH. Thus, these results for AB plate material indicate that an interaction occurs with the sample when an Fe(II)-based reductant is used which not only yields artificially low Ni(III) values, but also leads to an unusual level of metallic iron in the particulates which are removed with the stirbar.

CONCLUSIONS

The inquiry into the role of an iron (II) based reducing agent, in the form of ferrous ammonium sulfate or other ferrous-type reductants, shows that this cationic species leads to artificially low results in an analysis for nickel precharge in positive plates from nickel/cadmium cells. The substitution of a tin (II) species in the compound stannous chloride gives more acceptable values, in terms of what might be expected from manufacturing requirements.

A great many questions remain to be resolved about this analysis, for the nature of the interaction between Fe(0, II, and III) and permanganate which leads to the low Ni(III) analyses, and which facilitates solution of metallic iron, cobalt, and nickel, needs to be understood. Also, it is puzzling how the NiOOH retains its stability during the reduction step in dilute acetic acid. Some answers may be provided if known Ni(III) or Ni(IV) content materials could be used as standards. It is hoped that this work can be extended in order to answer these questions. In the meanwhile, use of stannous chloride as the reducing agent in the determination of nickel precharge appears to be a recommended alternative to the standard procedure.

Nickel-Hydrogen Technologies Session

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