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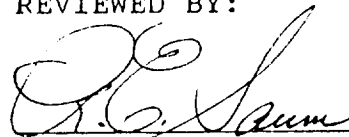
REPORT OF INVESTIGATIONS
INTO CHARGE CADMIUM
REACTIVITY: NICKEL-CADMIUM CELL
ESD 91-86
19 SEP 1991

PREPARED BY:



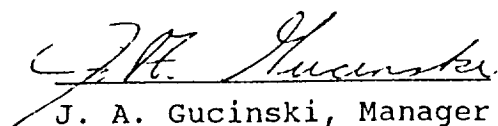
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REPORT OF INVESTIGATIONS INTO
CHARGED CADMIUM REACTIVITY:
NICKEL-CADMIUM CELLS

Ref: (a) Comparison of Physical and Chemical States of Two Separator Type Ni-Cd Cells From a Satellite Simulation Program, Presentation at 25th Annual IECEC Meeting

1. Introduction.

a. In August 1990, a presentation was given, reference (a), at the 25th Annual IECEC meeting in Reno, Nevada on the results of Destructive Physical Analysis (DPA) on two successive sets of Ni-Cd cells. The cells were of two different separator types, Pellon 2505 and 2536. One cell of each separator type was analyzed on two occasions; the first pair were analyzed October-November 1988 to establish baseline data on essentially new cells; the second pair were analyzed in January-February 1990 after the cells had been on charge-discharge cycling for a year in connection with a satellite simulation study at Naval Weapons Support Center Crane (NWSCC).

b. During the report presentation, several questions arose concerning the gas composition found in the cells, the absence of charged cadmium in the analytical data presented, and the appearance of dried-out portions on the Cd plates in the one-year cell S/N 7 which utilized Pellon 2505 as its separator material. It is the intention of this report to respond to the stated concerns and to clarify the observational results.

2. Procedures.

a. Gas Compositions. The data presented in reference (a) for gas compositions in the cell head spaces were given as percent of total, and it was stated that the actual cell pressures were much less than one atmosphere. In the Results section following, the original data are converted to mole quantities for clarification.

b. Cadmium Analysis. The absence of residual quantities of cadmium metal in the analytical data from the anode analysis utilizing the 1980 Revision A NASA Goddard¹ procedure for DPA has been studied through several experiments. First, attempts have been made to cause reaction between Cd metal in potassium hydroxide (KOH) solution and ambient air. Second, the possibility that Cd metal may have dissolved during the first stage of the analysis scheme was investigated by subjecting Cd metal to the reagent conditions used to separate discharged from

charged Cd in the DPA procedure. Third, a set of nine 1/2 AA Ni-Cd cells was divided into three sets of three each and analyzed as follows:

(1) Three cells were opened in an inert atmosphere chamber under argon (Ar) containing < 0.2ppm oxygen. The negative plates were immersed in water which had been previously sparged with Ar and frozen before transfer into the chamber. The resealed container was removed from the chamber and the negative plates were immediately transferred to an Ar purged soxhlet extractor where they were extracted by Ar sparged water until the extractate tested neutral. The plates were then transferred immediately to an Ar-purged vacuum drying oven and dried at reduced pressure under an Ar leak at ambient temperature. Subsequently, the analysis for charged and discharged Cd was performed.

(2) Three more cells were opened, this time in the glove box, in a manner which would allow the greatest likelihood for reaction of charged Cd with air. The glove box was first purged with an N₂ flow for 30 minutes. The cells were opened and the negative plates placed in 400ml of de-ionized (DI) water which had not been previously sparged, then rinsed and placed in a second 400ml of DI water. These plates in water were then brought out of the glove box and allowed to stand in ambient air for >48 hours. Next, they were placed in an N₂ purged soxhlet extractor in ordinary DI water and extracted until the extractate tested neutral. These plates were then dried in an unpurged vacuum oven at reduced pressure under an Ar leak at ambient temperature and subsequently analyzed for charged and discharged Cd.

(3) The last three cells were treated as in paragraph (1) through the drying stage. At that point, the negative plates were cut in half and one-half of each plate was immersed in 31 percent KOH and heated at 70 to 75C for 20 hours with pure O₂ bubbling through the solution. The intent was to provide insofar as possible a ready environment for alkaline solution oxidation of residual Cd in the plates. After this treatment, the plates were extracted and dried as before, and analyzed along with the control half-plates for charged and discharged cadmium. The nickel plates from the cells utilized in this paragraph were treated exactly the same to determine whether the nickel in the Ni(OH)₂ state could be reoxidized to NiOOH or NiO₂. These plates were then analyzed for charged and discharged nickel material, using the unreacted half-plates as controls.

c. Separator Characterization. To determine whether the cells S/N 7 and 9 were interchanged during teardown so that the dried-out Cd plates were identified with incorrect separator material, an infrared analysis of the separators was performed for materials from the four cells analyzed thus far.

3. Results and Discussion.

a. Gas Composition. With respect to the gas analyses, the following data were presented in the original paper:

Gas Sampling	S/N 28 Pellon 2536	S/N 9 Pellon 2536	S/N 95 Pellon 2505	S/N 7 Pellon 2505
Cell History	Baseline	One Year	Baseline	One Year
% H ₂	53.64	18.44	17.84	17.34
% He	14.48	6.97	33.08	24.81
% N ₂	30.45	62.95	48.44	55.74
% O ₂	1.43	11.64	0.64	2.11

These were the gas chromatographic compositional analyses in percent of the gases present in the cell head space. The gas chromatographic technique uses a thermal detector response. Argon is used as the carrier gas to allow a clean measure of the four components. We take one example of composition, and convert it to an approximate amount of gas present using rather generous estimates in order to develop maximum gas quantity calculations:

In S/N 28, the recorded pressure was 150.4 torr. The gas expands into an evacuated fixture of approximate volume 2-3cc. The free volume in the cell can is about 5-8cc. The increase in available volume is thus about 33 percent for a maximum total volume of about 10cc. Then an estimate of the original pressure in the can would be 150torr x 4/3 = 220torr. Next, using $n = \frac{PV}{RT}$ to calculate a mole quantity gives

$$n(\text{H}_2) = \frac{(2 \times 10^2 \text{ torr} \times 0.5364) \times 10 \text{ cc}}{6.24 \times 10^4 \text{ cc torr K}^{-1} \text{ mol}^{-1} \times 3 \times 10^2 \text{ K}} = 5.7 \times 10^{-5} \text{ mol}$$

for hydrogen gas. Similar calculations for all components yields the following:

Gas Sample	S/N 28	S/N 9	S/N 95	S/N 7
Measured P	150 torr	280 torr	380 torr	530 torr
Moles H ₂	5.7x10 ⁻⁵	3.7x10 ⁻⁵	4.8x10 ⁻⁵	6.6x10 ⁻⁵
Moles He	1.5 x10 ⁻⁵	1.4x10 ⁻⁵	8.9x10 ⁻⁵	9.4x10 ⁻⁵
Moles N ₂	3.2x10 ⁻⁵	1.3x10 ⁻⁵	1.3x10 ⁻⁴	2.1x10 ⁻⁴
Moles O ₂	1.5x10 ⁻⁶	2.3x10 ⁻⁵	1.7x10 ⁻⁶	8.0x10 ⁻⁵

From these data the following observations may be inferred:

(1) The actual quantities of gases present in the cell are very small.

(2) The amount of hydrogen observed is about constant.

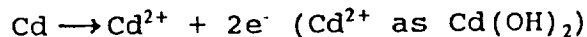
(3) The helium is probably present because it was inserted for leak detection.

(4) If no purging or back flushing is performed, then the nitrogen present is residual from the air evacuation and the amounts are not unusual.

(5) The amount of oxygen observed has increased with cycling. In fact, if the N_2 present is residual from the evacuation of air, then the O_2 content should be about 20 percent of N_2 . For S/N 28 and 95, O_2 is much less than 20 percent of N_2 , while in S/N 7 it is about 2X and in S/N 9 very much larger than the natural O_2/N_2 ratio, indicating an initial (baseline) O_2 depletion and then accumulation during cycling.

b. Limiting Electrode. A statement in reference (a) that the cells were negative plate limited was a cursory observation based on the analytical evidence that the discharged cells still contained NiOOH but no residual Cd. This was a too casual conclusion. In fact, the cells are manufactured to have an excess of Cd (positive limited). A more thorough review of the analytical data gives the following results:

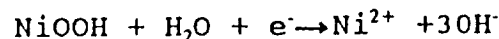
Each cell contained 11 positive and 12 negative plates. The analytical weights of $Cd(OH)_2$ from three plates in S/N 28 for example were 7.84g, 8.40g, and 8.49g, giving an average of 8.24g $Cd(OH)_2$ per plate. For 12 plates this is about 100g $Cd(OH)_2$. The cell reaction on discharge is



so the recovered cadmium hydroxide converts as

$$100g \text{ Cd(OH)}_2 \times \frac{1 \text{ mol Cd(OH)}_2}{146.4g \text{ Cd(OH)}_2} \times \frac{1 \text{ mol Cd}}{1 \text{ mol Cd(OH)}_2} \times \frac{2 \text{ mol } e^-}{1 \text{ mol Cd}} = 1.37 \text{ mol } e^-$$

For nickel, three plates analyzed of the eleven present gave an average of 5.38g $Ni(OH)_2$ and 0.662g NiOOH. For eleven plates in the cell there were 59.2g $Ni(OH)_2$ and 7.28g NiOOH total. The reaction is



and so the reduced $Ni(OH)_2$ has consumed

$$59.2\text{g Ni(OH)}_2 \times \frac{1\text{mol Ni(OH)}_2}{92.7\text{g Ni(OH)}_2} \times \frac{1\text{mol NiOOH}}{1\text{mol Ni(OH)}_2} \times \frac{1\text{mol e}^-}{1\text{mol NiOOH}} = 0.639\text{mol e}^-$$

while the remaining NiOOH would consume

$$7.28\text{g NiOOH} \times \frac{1\text{mol NiOOH}}{91.7\text{g NiOOH}} \times \frac{1\text{mol e}^-}{1\text{mol NiOOH}} = 0.0729\text{mol e}^-$$

for a total of 0.718mol e⁻. The ratio of Cd to NiOOH is almost 2:1 in terms of electron exchange, so the positive electrode (Ni) should be the limiting electrode. However, if upon complete discharge of a cell no Cd is found during DPA, but NiOOH is observed, then it is probable that the cell would have behaved as though it was negative plate limited if driven to reversal.

c. Cadmium Reactivity. The previous calculations raise an immediate question as to why no cadmium metal was found in the analysis. There are several possible explanations:

(1) Cd metal could dissolve in the electrolyte once air is admitted to the cell. It has been observed in these labs that the Cd plates from AA-size cells become warm to the touch during cell disassembly in ambient air and it is known that Zn plates from Ag/Zn batteries will ignite in air if saturated with KOH. The Ni and Cd plates within the cell are exposed to an air atmosphere once the cell has been tapped for gas analysis, and transfer to a nitrogen-purged glove box occurred immediately after gas sampling. Cotton and Wilkinson² state that Cd does not react directly with alkaline solutions because Cd is not amphoteric like Zn; Cd cannot form the cadmate analog to the zincate ion (ZnO₂²⁻). However, Cd(OH)₂ apparently does dissolve in concentrated alkali as a [Cd(OH)₄]²⁻ ion. Mellor³ reports that Cd forms Cd(OH)₂ in moist air. The conversion Cd → CdO → Cd(OH)₂ → [Cd(OH)₄]²⁻ is thus possible. However, when tests were performed in this lab where mossy Cd was immersed in 36 percent KOH and allowed to stand in contact with ambient air for two hours, the samples showed no significant weight loss for Cd. Nevertheless, the observation that plates coated with concentrated KOH and exposed to ambient air become warm indicates that a chemical reaction does occur, and electrochemically prepared Cd may be reactively different from the chemically prepared Cd which was used in these tests.

(2) Cd metal may be attacked by the solution of ammonium acetate in ammonium hydroxide designed to separate Cd(OH)₂ (discharged material) from Cd metal (charged material) in the negative plate. Again, it is known that Zn plates from silver-zinc batteries suffer the problem of solution of Zn in ammonium acetate-ammonium hydroxide solution. However, when mossy Cd metal was stirred with heating for 2 hours at 80C in the solution designed for the separation procedure, no weight reduction was observed for Cd metal. Consequently, it does not

appear that this explanation will account for the absence of charged Cd either.

(3) In the GSFC-DPA procedures¹ no reagent blank is specified in the Cd metal titration. It has been found that a reagent error amounting to 60 to 70 percent of the total titer for Cd metal must be accounted in this analysis. This would explain why some analysts might report Cd presence from this procedure if it is determined in an analysis where reagent blank corrections are not utilized.

(4) The total Cd analysis performed for the four cells analyzed thus far has accounted for 97 to 99 percent of the weight recorded for the whole plate, for a total of 12 plates analyzed. If a significant analytical error were occurring where Cd metal was being accidentally analyzed as Cd(OH)₂, then the total analytical weight would be greater than the actual plate weight by 10 to 15 percent at least, since two hydroxy groups are 30 percent of the weight of cadmium. But in fact, in all the cells analyzed, the accumulated weight did not vary from the actual weight by more than +3 percent and in some cases the variation was negative.

d. Cadmium Analysis. The next step was to determine whether charged Cd could be found if Cd plates from another cell type which were known to contain excess charged Cd were dissected and great care were taken to exclude air during cell dissection and plate handling up through the soxhlet extraction of KOH. The procedure is described in Section 2b(1). The analytical results, following that procedure, are as follows:

Cell Number	Discharged Cd (g)	Charged Cd (g)	Total Cd (g)	Charged Cd (%)
11	2.4960	0.1009	2.5969	3.88
15	2.3521	0.0934	2.4455	3.82
17	2.5026	0.1262	2.6288	4.80

* 1/2 AA-Size

Next, the experiment was repeated using the procedure in 2b(2). In this case, the data obtained are:

Cell Number	Discharged Cd (g)	Charged Cd (g)	Total Cd (g)	Charged Cd (%)
22	2.4788	0.1209	2.5997	4.65
23	2.5518	0.1199	2.6717	4.49
24	2.6090	0.1083	2.7173	3.99

* 1/2 AA-Size

From these data, it appears that the consequences of somewhat less than scrupulously oxygen-free handling prior to the soxhlet extraction has negligible effects upon the presence of charged Cd.

(1) Then the obvious question which follows is whether a reaction of charged Cd in the plate with oxygen can be forced to occur at an appreciable rate. To test this, the procedure in 2b(3) was utilized. The results of the analysis on the respective samples are:

Cell Number	Discharged Cd (g)	Charged Cd (g)	Total Cd (g)	Charged Cd (%)
27	2.5434	0.0589	2.6023	2.26
27 <u>w</u> O ₂	2.4202	0.0382	2.4584	1.55
28	2.5416	0.0760	2.6176	2.90
28 <u>w</u> O ₂	2.4497	0.0169	2.4666	0.69
30	2.5707	0.0602	2.6309	2.29
30 <u>w</u> O ₂	2.4613	0.0518	2.5131	2.06

* 1/2 AA-Size

It appears from these data that although there is a decrease in the Cd content upon reaction of the plate with O₂ in alkaline solution, the reaction is not rapid. Therefore, on the time scale associated with cell teardown and removal of plates to soxhlet extractors, casual exposure to ambient air would not cause total depletion of charged Cd present in the plates. Further, from the variation in Cd composition over the nine 1/2 AA cells analyzed, it seems evident that the formation of charged Cd during plate preparation and cell assembly and conditioning is inexact and non-reproducible.

(2) During the previous studies, two approaches were taken to the removal of negative plate material from the grids. In one set of samples, the entire sample, grid included was dissolved in nitric acid. Then both samples were treated according to standard methods for DPA¹. The following table presents the analytical results:

Cell Number	Sample w Grid Charged Cd (%)	Sample wo Grid Charged Cd (%)	Difference (%)
15	2.28	3.82	40.3
17	3.18	4.80	33.8
22	2.37	4.65	49.0
23	1.95	4.49	56.6
24	1.69	3.99	57.6
27	0.55	2.26	75.7

As can be seen, those samples where the grid was dissolved with the charged Cd exhibited significantly lower Cd content than those where the charged Cd was removed from the grid prior to solution and analysis. The grid material is nickel plated iron wire and in the analytical scheme the acid solutions are adjusted to pH 10 prior to determination of Cd content. At that pH, iron forms a very gelatinous precipitate which occludes the Cd²⁺ ions, even after repeated washings to a filtrate volume of 500ml. Thus an analytical procedure which requires solution of grid substrate containing iron will inherently lower the amount of charged Cd found during analysis.

e. Nickel Reoxidation. A final question which arose during the attempted oxidation of Cd with O₂ was whether Ni(OH)₂ could be reoxidized to NiOOH or NiO₂ in alkaline solution. A procedure similar to that for Cd was used for the positive plates of two cells to investigate this possibility, and the data are reported in the following table:

Cell Number	NiO ₂ (%)
28	0.09
28 w O ₂	7.02
30	0.09
30 w O ₂	7.51

It appears that oxidation of Ni(OH)₂ is not only possible, but relatively easy. Consequently, any weight gain observed for a whole cell if O₂ is deliberately used to estimate residual Cd in that cell before DPA may just as well be due to nickel re-oxidation. And in fact, the possibility that iron in the grids can be converted to Fe₂O₃ must also be considered, and we have obtained some evidence which suggests that occurs as well.

f. Analysis Summary. In summary, the following statements may be made:

(1) If there is residual charged Cd in a cell, it does not react so easily with ambient air under alkaline conditions that analysis should give zero Cd. In the original analysis of cells with S/N's 28, 95, 7, and 9, the individual cell results were:

Cell Number	Plate Number	Charged Cd (g)	Charged Cd (%)
28 (2536)	3	0.0	0
	9	0.0	0
	13	0.0	0
95 (2505)	3	0.0	0
	9	0.0	0
	13	0.0	0
9 (2536)	3	0.026	0.36
	9	0.093	1.27
	13	0.298	3.77
7 (2505)	3	0.0	0
	9	0.0	0
	13	0.011	0.15

Only in cell S/N 9 were significant quantities of Cd metal found. It is concluded that the other three cells did in fact have no significant residual Cd. It is important to state that all four cells were handled in identical manner during DPA procedures prior to the soxhlet extraction of KOH from the alkaline-soaked plates.

(2) Suggestions have been made that residual Cd could be estimated from cell weight gain as a consequence of deliberate oxidation of the negative plates while still in the cell. There appears to be good evidence that such weight gains may just as well be attributed to reoxidation of discharged Ni materials, and perhaps also of Fe in the grids.

(3) Care must be taken with regard to Cd²⁺ occlusion in gelatinous Fe₂O₃ · xH₂O formed when the entire negative grid and plate material are dissolved in nitric acid in the charged Cd analysis procedures.

g. Infrared Characterization of Separators. The infrared scans of the two separator materials, Pellon 2505 and 2536, are very similar, as expected. However there is a prominent peak at 934cm⁻¹ in the 2536 spectrum which is absent from the 2505 spectrum. The spectra of S/N's 28 and 9 both exhibit this peak,

and have been identified throughout the analyses as Pellon 2536, while spectra of S/N's 95 and 7, which have been identified with Pellon 2505, are missing this peak. There are, in addition, position shifts in peaks in the 2505 material at 1263, 1170, and 1122 cm^{-1} , to 1274, 1180, and 1146 cm^{-1} respectively for 2536 which are consistent in both separator sets identified by S/N's 2505 and 2536. Thus, that separator material identified with S/N 7 in which the Cd plates had appeared dried out and discolored is unambiguously Pellon 2505.

Conclusions.

a. As a consequence of the presentation discussed in the introduction to this report, four areas of concern arose in the Ni-Cd community with regard to the reported DPA results on the first four nickel-cadmium cells from a satellite simulation study analyzed at NWSCC in 1988-1989 and 1989-1990. An investigation of the procedures and results which were the basis of those concerns has been completed and the results have been detailed in the preceding sections. The analytical problems and their resolution were developed as follows:

(1) The analysis data of head space gases for the four cells have been converted to mole quantities, using estimations of the head space and sampling device volumes. These are within ten percent of actual volumes but are deliberately estimated large. From the data it can be concluded that the analytical values were consistent with expectations based on the cell preparation procedures and subsequent cycling history.

(2) Calculations based on the analytical values of cadmium and nickel contents of one of the four cells have shown that the mole ratio of cadmium to nickel, in terms of electron exchange, is about 2:1. Therefore, the cells were constructed to be nickel (positive electrode) limiting. But in fact in three of the four cells no residual (charged) cadmium metal was found after complete discharge, while residual NiOOH was found in significant quantities. Indeed, even in the single cell where residual Cd was found, the ratio of residual NiOOH to Cd was 4:1 based on moles of electrons. Consequently, even if the cells were manufactured to be cadmium-rich, if driven to reversal, they would operate as if they were negative-limited.

(3) Several of the steps in the DPA procedure¹ were examined to determine whether Cd metal could be converted to Cd(OH)₂ or CdO₂ prior to the analytical processes for its determination. The results were negative in the sense that the actual procedural steps did not appear to be at fault.

(4) Next, several Ni-Cd cells of another size which were known to contain residual Cd at full discharge were analyzed after being subjected to conditions where it was possible for Cd

to be oxidized to Cd^{2+} prior to the chemical characterization. Only in circumstances where the negative plates were deliberately oxidized for 24 hours in alkaline solution at elevated temperature was a decrease in the Cd content observed in comparison electrode strips. Even then, residual analyzable Cd was still present in significant quantities.

(5) During these last studies, it was found that the DPA procedure incorporated an inherent loss of analyzable Cd if grids with significant iron content were dissolved in acid during the analysis. In that event, gelatinous $Fe_2O_3 \cdot xH_2O$ occluded 25-50% of the Cd^{2+} , preventing its determination. Also, it was found that deliberate attempts to oxidize Cd to Cd^{2+} while the plates were still in the cell may result in reoxidation of $Ni(OH)_2$ to $NiOOH$, and of iron to Fe_2O_3 .

(6) Therefore, if NiCd cells contain residual Cd at complete discharge, the DPA procedure should detect it. Moreover, exposure of the alkaline cell pack to ambient air for periods up to 24 hours should not reduce the Cd content to zero.

(7) With respect to the stated observation that cell pack S/N 7 with Pellon 2505 separator exhibited drying of some plates and consequent darkening of the negative plates, it has been confirmed that this observation was correctly attributed. The separator materials, 2505 and 2536, have sufficiently different IR spectra to allow unambiguous identification. The plates and separators were placed in similarly marked zip-lock bags during the dissection, extracted to remove KOH simultaneously, and then placed in fresh, similarly marked zip-lock bags and stored over desiccant until analyzed. Since each cell was dissected and packaged separately, the separator materials serve as a positive identifier of the cell of origination. Infrared reanalysis has confirmed that S/N 7 did indeed contain the 2505 separators.

b. In summary, the data and discussions submitted to the Reno, Nevada IECEC Meeting (1990) by NWSCC were representative of the DPA procedures utilized, and were correct with respect to analytical results. If misunderstandings arose as a consequence of the manner in which the data were presented, they should be ascribed to the fact that these space satellite cells were the first complete DPA analyses performed by the Material Sciences Lab personnel on the nickel cadmium chemistry.

5. Recommendations. In order that the previous results may be unambiguously tied to the Navy Navigational Satellite cells, two tasks should be undertaken:

a. A third set of cells from the NWSCC simulation study, one of each separator type, should be subjected to DPA procedures

utilizing the tightest possible control over the cell tear-down, including gas sampling, by conducting the operations in an argon atmosphere dry-box. Such a procedure would also lay to rest any doubts regarding the gas sampling procedure because if the fixture leaks during sampling, argon would become a major constituent of the gas analysis. The gas analysis procedures will be modified to detect Ar contamination.

b. Two fresh cells of either separator type with "excess" charge should be made available by the manufacturer of the original cells for DPA. These would be conditioned by several charge/discharge cycles, then discharged for DPA. One would be subjected to rigorously secure DPA, the other opened in ambient air, allowed to stand open to air for 24 hours, then disassembled under inert atmosphere conditions. One-half the cadmium plates from each cell would be subjected to immediate analysis while the other half would be allowed to stand wet with KOH in ambient air for another 24 hours prior to analysis. The objective would be to determine whether significant analytical cadmium content changes could be found in these plates as a consequence of ambient air handling. These recommended tests should finally establish the veracity of the DPA procedures performed and the results reported by the Material Sciences Laboratory in Code 305 at NWSCC.

6. Bibliography.

a. Halpert, G and Kunigahalli, V., "Procedures for Analysis of Nickel-Cadmium Cell Materials", Document X-711-74-279, Revision A, December 1980, NASA Goddard Space Flight Center, Greenbelt, MD 20771.

b. Cotton, F.A. and Wilkinson, G., Advanced Inorganic Chemistry, John Wiley and Sons, New York (1980), 592-600.

c. Mellor, J.W., Inorganic and Theoretical Chemistry (IV), Longmans, London (1963), 472-73.

Cadmium Issue Panel Discussion

The following section contains input from the various participants in the panel discussion. Some of the materials submitted are the actual charts or speech that was used during the discussion; other materials are copies/summaries of related letters submitted by the individuals that summarize their points made during the discussion.

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The following is a brief summary of NASA's position with respect to the cadmium issue.

The proposed regulation by the Occupational Safety and Health Administration (OSHA) on the permissible exposure level (PEL) to cadmium has the potential to adversely affect NASA flight programs. This is due to the high dependence on cadmium for flight batteries in many NASA programs. For the past 25 years, nickel-cadmium (Ni-Cd) batteries have been the energy source for a vast majority of NASA missions. Ni-Cd technology also is currently planned for use on many future missions.

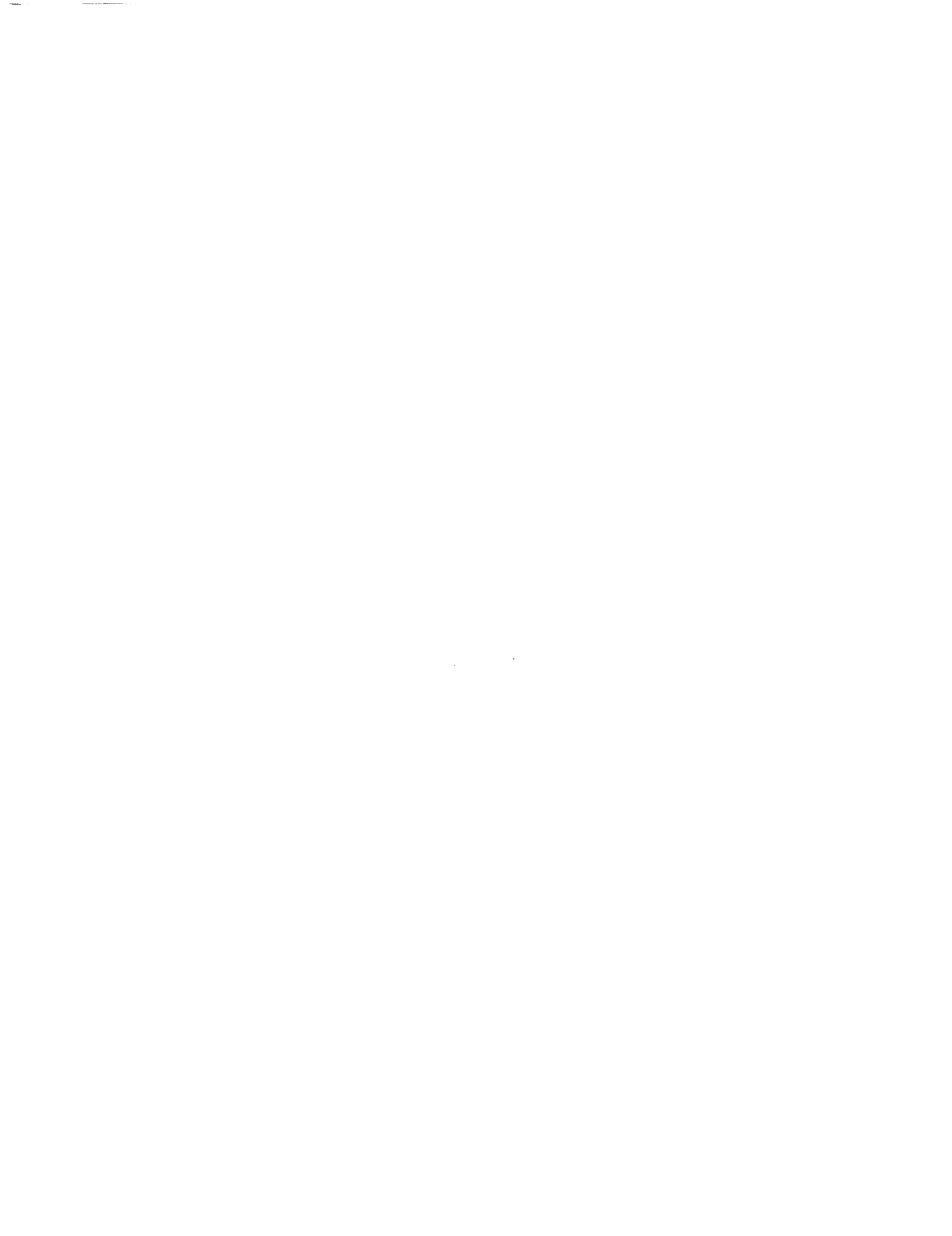
The only qualified supplier for NASA Standard Ni-Cd batteries has just recently announced it will cease production of these cells in the United States if the PEL is enacted as proposed. If this takes place, there will be no alternative but to consider other less-desirable options. One option is to develop new technologies such as nickel-metal hydride as a Ni-Cd replacement. This has risks similar to those of any development program: spacecraft redesign may be required, schedule delays may occur, development costs may be unexpectedly high, and successfully qualifying the technology is anything but assured. Another option would be for NASA to procure Ni-Cd batteries from foreign suppliers. Due to going to a new supplier, this option would have similar schedule, development cost, and success risks as if developing a new technology.

Also, the proposed PEL would hamper NASA's ability to internally analyze problems that may result from manufacturing errors or test failures. Because the analysis process, in part, requires the cutting and slicing of the cadmium plates, a PEL enacted at the proposed level would severely complicate the procedure. This type of analysis is critical to understanding problem causes and formulating potential resolutions.

NASA is also concerned that proposed PEL values would make it difficult to obtain qualified cadmium plated fasteners and seals that are presently designed into launch vehicle and spacecraft systems. In the past, counterfeit fasteners have been difficult to detect. Forcing NASA to look at foreign suppliers for this type of fastener will only increase the difficulty in controlling the use of counterfeit fasteners.

In conclusion, the proposed PEL of $1 \mu\text{g}/\text{m}^3$ or $5 \mu\text{g}/\text{m}^3$ would significantly impact NASA battery systems. Our ongoing Aerospace Battery Program addresses alternate secondary power sources to replace Ni-Cd; however, new space-qualified power sources will not be available until the late 1990's. Whatever direction NASA takes based on the OSHA ruling, there will be continued emphasis on providing safe, reliable, and high quality batteries.

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WILSON & WILSON

June 24, 1991

The Honorable J. Danforth Quayle
Vice President of the United States
Old Executive Office Building
17th Street and Pennsylvania Avenue, NW
Washington, DC 20501

Dear Mr. Vice President:

I am writing to ask that you consider utilizing the President's Council on Competitiveness and the National Space Council to review a proposed regulation from the Occupational Safety and Health Administration (OSHA) concerning cadmium, a metal considered vital by NASA, the White House Office of Science and Technology Policy and several other agencies of the Executive Branch.

I, along with representatives from my client, The Cadmium Council, have previously met with Mr. David McIntosh and Ms. Nancy Mitchell of your office concerning this matter.

Cadmium is an inevitable co-product of zinc production and is used in nickel-cadmium batteries, as a pigment or as a heat and weathering stabilizer in engineering plastics, and as a corrosion-resistant coating in aerospace, electronic and industrial applications. Cadmium compounds also play important roles in advanced detector systems, imaging sensors and photovoltaic energy devices.

The Cadmium Council, which represents the North American cadmium industry, is deeply concerned with OSHA's proposed rule for occupational exposure to cadmium, which was published in the February 6, 1990 Federal Register. If implemented, the proposed rule will most likely result in the demise of the domestic cadmium industry and will have serious economic consequences for many other major industries.

Public comments filed by the Office of Management and Budget, the Department of Commerce, the Department of Interior, the Bureau of Mines, the Small Business Administration and NASA all indicate severe consequences if OSHA is successful with its proposed regulation. Cadmium is also mentioned eight times in the report recently filed by the National Critical Technologies Panel, a study which identifies important technologies and materials which are crucial to their development.

The heart of our concern with OSHA's proposal is that it violates the Occupational Safety and Health Act, which states that OSHA may adopt a standard only if it is technologically and economically feasible for affected industries to meet the standard.

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The Honorable J. Danforth Quayle, Page Two.

All of the federal bodies mentioned above believe OSHA has failed that crucial test. After several meetings with OSHA, it appears that OSHA itself agrees that the industries cannot meet the levels put forth in their proposal through engineering controls and work practices. However, OSHA has proposed standards of either 1 or 5 micrograms of cadmium per cubic meter of air, well below the level of 50 micrograms per cubic meter currently considered generally feasible in the industry.

OSHA's approach will create international competitiveness inequities and is contrary to current case law. The Cadmium Council believes that the effects upon employment and the balance of trade deficit will be substantial if OSHA is successful in implementing this new regulation.

Independent studies predict that imposition of the new OSHA standards would result in the closure of three U.S. nickel-cadmium battery manufacturing facilities comprising 55% of U.S. sales and 99% of U.S.-owned facilities, with the loss of more than 2300 jobs in the United States.

In addition, because the U.S. firm which manufactures over 90% of all nickel-cadmium battery cells for space vehicles and satellites would be among those closed, power supplies for the U.S. civilian and military space effort would have to be obtained, if possible, from foreign suppliers, further contributing to employment and trade losses.

The cost impact of the proposed rule would result in almost all U.S. nickel-cadmium batteries being manufactured off-shore, following the example of VCR's and other small electronic products.

As for the health risk argument, OSHA has developed risk assessments for cancer and renal dysfunction which the Office of Management and Budget has criticized as unreasonable.

Finally, OSHA has ignored the fact that most other industrialized nations have cadmium health standards in the range from 20 to 50 micrograms per cubic meter and that with those standards in place, no major health problems have been observed.

Toward that end, members of The Cadmium Council and other major trade associations would appreciate any action you, the Presidents' Council on Competitiveness or the National Space Council might take to urge OSHA to follow its legal guidelines.

Respectfully Submitted,



ROBERT DALE WILSON
Attorney At Law

CC: Mr. John Sununu
Mr. Alan Hubbard

GATES ENERGY PRODUCTS

BACKGROUND

- CURRENT OSHA EXPOSURE LIMIT IS 200 ug/m³ -- ESTABLISHED IN 1972
- GEP -- AND OTHER NiCd BATTERY MAKERS WORLD-WIDE -- ARE GENERALLY ENGINEERED TO 50 ug/m³
- OSHA'S PROPOSED RULE-MAKING WOULD IMPOSE A MAXIMUM EXPOSURE OF EITHER 1 OR 5 ug/m³
- OSHA'S RULE-MAKING IS EXPECTED TO BE PROMULGATED IN Q1 OR Q2 OF 1992

MRH1

GATES ENERGY PRODUCTS

POSITION

- o GEP HAS TAKEN LEADERSHIP ROLE IN SEEKING A REASONABLE SOLUTION
- o COST TO ENGINEER PLANT TO 25 ug/m3 IS ESTIMATED TO BE AN ADDITIONAL:
 - \$20 MILLION CAPITAL
 - \$4 MILLION/YEAR OPERATING COST
- o MARGINS ARE UNDER SEVERE PRESSURE FROM FOREIGN COMPETITION; THESE COSTS WOULD MAKE US LESS COMPETITIVE
- o GEP IS NOT ABLE -- OR WILLING -- TO PAY THE ADDITIONAL COSTS TO MEET THE PROPOSED RULE, BASED ON SOUND BUSINESS PRACTICE
- o BOB SHILEY -- GEP PRESIDENT:
 - 'IF THE REGULATION IS ESTABLISHED AT EITHER OF THOSE LEVELS (i.e., 1 OR 5 ug/m3, GATES WILL CEASE PRODUCTION OF NICKEL CADMIUM BATTERIES IN THE UNITED STATES'
- o GEP REQUIRES A NUMERICAL WORKPLACE STANDARD TO ALLOW US TO CONTINUE IN BUSINESS, OR SUFFICIENT TIME FROM OSHA TO PHASE OUT OF THE MANUFACTURE OF NiCd BATTERIES
- o GEP IS DEVELOPING STATE-OF-THE-ART NIMH CELLS, AND CONVERTING FROM NiCd TO NIMH

MRH2

GATES AEROSPACE BATTERIES

- (IF RULE IS ESTABLISHED AT LESS THAN 50 ug/m3)
- o GAB IS SUBJECT TO SAME CONSIDERATIONS AS GEP -- ADDED COSTS WILL MAKE US UNCOMPETITIVE
 - o GAB WILL NOT MANUFACTURE NiCd CELLS AFTER GEP HAS PHASED OUT OF NiCd
 - o ACTIVATION (FROM DRY STORAGE) OF WELDED CELLS DOES NOT PRESENT A CADMIUM HAZARD -- DRY STORAGE COULD PROVIDE A SCHEDULE BUFFER
 - o OSHA RULE-MAKING THREATENS GAB'S ABILITY TO PROVIDE CONTINUING SUPPLY OF NiCd CELLS
 - o CUSTOMERS ARE ADVISED TO WATCH THE RULE-MAKING CLOSELY TO ENSURE THAT THEIR PROGRAM NEEDS ARE COVERED:
 - ACCELERATE PRODUCTION AND DRY STORE (IF OSHA ALLOWS TIME)
 - OTHER SOURCES (FOREIGN)
 - OTHER COUPLES - NiH2
 - NiMH
 - o GATES AEROSPACE BATTERIES IS DEVELOPING NiMH CELLS TO REPLACE NiCd AEROSPACE CELLS -- RESULTS ARE VERY ENCOURAGING -- PAPER LATER TODAY

MRH3

1991 NASA AEROSPACE BATTERY WORKSHOP

ROLAN C. FARMER, OPERATIONS MGR.
EAGLE-PICHER INDUSTRIES, INC.
COLORADO SPRINGS, CO

CADMIUM ISSUE & NICKEL-CADMIUM BATTERIES

• BACKGROUND:

1. All EPI Ni-Cd Battery Business consolidated at Colorado Springs..
2. EPI builds 3 types of Ni-Cd's
 - a. Vented Ni-Cd
 - b. Sealed Maintenance-Free Ni-Cd's
 - c. Sealed Aerospace Ni-Cd's

• ENVIRONMENTAL REGULATIONS:

1. Clean Water Act - EPI has reduced process water discharge 90%. Current discharge is non-detectable in Cadmium.
2. R.C.R.A. disposal of spent batteries
 - a. EPI recycles all Cd material, therefore does not generate hazardous waste.
 - b. INMETCO currently accepts spent batteries as hazardous waste.
3. OSHA Workplace Standards
 - a. Due to be issued in early '92.
 - b. OSHA has reopened the rule making record.
 - c. May be two tier P.E.L. or possible exemption for plate making and assembly.

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▪ EPI NICKEL-CADMIUM PLANS

EPI's current plans are to continue in the Nickel-Cadmium business.

1. Standard issued in 82 will likely be phased in over 2-5 years.
2. Negative plate making and assembly might be exempt or the higher two tier approach accepted.
3. EPI will be able to meet a reasonable level for smaller markets such as Aerospace.

▪ ADVICE "DON'T PANIC" - CD IS NOT THE ONLY ISSUE

1. Lead levels are also proposed to be lowered.
2. Nickel has been listed as priority material by "Industrial Hygienists"
3. Most battery materials will eventually receive the same attention as Cadmium.

HUGHES EDD POSITION ON PROPOSED NEW OSHA
STANDARDS FOR AIRBORNE CADMIUM

I am David F. Pickett, Manager of the Energy Storage Product Line at Hughes Aircraft Company. We are a product line in the Electron Dynamics Division which is in the Industrial Electronics Group. Our mission is to supply high technology batteries and other energy storage devices and technology to other divisions and groups within Hughes Aircraft as well as General Motors, the U.S. Government and the aerospace industry. Our main customer is the Space & Communications Group (S&CG) at Hughes. Prior to January 1990 most of our organization was in S&CG. About two-thirds of our sales volume is directly related to Space hardware and about 20 to 30 percent of this volume is sales of nickel-cadmium batteries to either S&CG, Government agencies or other aerospace companies. It was our plan in moving from S&CG to acquire a source of nickel-cadmium, nickel-hydrogen and sodium sulfur cells either through business arrangements with other suppliers or to build the facility ourselves. In the past we fabricated our own nickel-hydrogen cells in-house, buying some piece parts such as nickel electrodes from other suppliers. We currently are building sodium sulfur cells. In the case of the nickel-cadmium technology, we still depend on outside sources to furnish us cells. Thus our business would be significantly affected should all nickel-cadmium suppliers go out of business because of the new OSHA 5 microgram per cubic meter of air borne cadmium standards.

Our position on nickel cadmium cell technology is quite unique compared the rest of the industry. We have our own technology which we have developed with our IR&D funding. We call it Super NiCd technology. We have agreements in place with Eagle Picher and Gates, who make cells for us using this technology. We also have an agreement with Eagle Picher whereby they build cells for us for sale to other aerospace contractors. We have not issued a license to anyone to manufacture or sell this technology without our involvement.

I personally have examined the testimony and exhibits listed in OSHA Docket H-057A and the reports generated by Pace Incorporated for the Cadmium Council and appreciate the conclusion that implementing the proposed new₃ requirements of 5 micrograms of cadmium per cubic meter (5 ug/m^3) would be expensive; however, detailed studies were not performed for a totally enclosed, low volume, aerospace flat plate nickel cadmium cell operation. The studies address mainly wound cell plant operations of a high volume level. Before we could come to any cost figures on a totally enclosed aerospace line, we would need to look at this very closely. We have performed no

detail studies as yet. We have been hopeful that our sources of nickel cadmium cells will stay in business. If they don't then we will have to reconsider our position.

Should we make a decision to go into limited production of nickel cadmium cells for space applications, we have a number of strong points which could be of consideration. Our facility in Torrance, California has been manufacturing traveling wave tubes for satellites and military applications for well in excess of 25 years, and cryogenic coolers and aerospace quality heat pipes for about 10 years. We not only have to adhere to very strict aerospace standards and particle controls for these products but have to comply with environmental regulations in the Southern California area such as those imposed by the Air Quality Management District (AQMD), Proposition 65 and the like. We think we could probably make nickel cadmium cells and satisfy the newly proposed OSHA air borne cadmium requirements. We have not concentrated our efforts into designing a nickel cadmium facility, as yet, in Torrance but very likely may do so if our sources threaten to disappear.

Starting any off shore operations with a facility which exceeds the new OSHA air borne cadmium requirement is simply out of the question for us for numerous reasons. First of all we could not, in good conscience, let any subcontractor employees work under standards inferior to those imposed by Hughes in the U.S. In offshore operations which we currently maintain, Hughes and OSHA type standards are still the enforced rule. Going around the regulation also implies that we do not agree with the health risks and are imposing our own standards. We are not qualified to do this.

Advanced Technologies Session

*Organizers: Sal Di Stefano
Jet Propulsion Laboratory*

*Ed Buzzelli
Westinghouse Science & Technology Center*

