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TEMPLE UNIVERSITY
OF THE COMMONWEALTH SYSTEM OF HIGHER EDUCATION
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DEPARTMENT OF GEOLOGY
D. E. Grandstaff

TITLE ON PAGE 8

May 20, 1982

WM Record File 101
WM Project 10
Docket No.
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for. Cook to Knapp

Dr. Mick Apted
Rockwell Hanford Operations
Energy Systems Group
P. O. Box 800
Richland, WA 99352

Dear Mick,

Please find enclosed copies of the monthly report for May 20, 1982, a copy of the gold inventory letter to Darlene Schatz, and a copy of the abstract which we are submitting to the GSA meeting in New Orleans. Gene talked to Mike Smith about the abstract and received preliminary oral permission to send it. If there are any reservations about the abstract it can, naturally, be withdrawn.

If there are any questions, please contact us.

Sincerely,

Dave

WM DOCKET CONTROL CENTER

RECEIVED MAY 21 P.M. BWIP CORRESPONDENCE CONTROL

Permanent Record
JUL 16 1982
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Your Abstract Number No. 09608

NEW DEVELOPMENTS IN HYDROTHERMAL Eh-pH MEASUREMENTS

ULMER, Gene C., GRANDSTAFF, David E., and BROZDOWSKI, Robert A., Geology Department, Temple University, Philadelphia PA 19122; and BARNES, Hugh L., and BOURCIER, William L., Ore Deposits Research Section, The Pennsylvania State University, University Park, PA 16802

Recent investigations have attempted measurement and control of Eh and pH under conditions up to 300° C and 300 bars. Electrodes, specific for either gaseous or ionic hydrogen and/or oxygen, have been investigated for Nernstian response to given activities or fugacities. Electrodes composed of organic polymers or ZrO_2 show great promise.

In this P-T range, the most successful pH cells have been constructed from Y_2O_3 stabilized ZrO_2 with various reference electrodes such as Ag-AgCl or Cu-CuO, very similar to those of Danielson (1979), MacDonald et al. (1978,79,80), and Niedrach (1980,81). Linear relationships between pH and emf have been achieved up to 573°K and 0.3 kb. Previously, ZrO_2 sensors had to be individually tested as most did not give Nernstian response. Tests show that only those electrodes whose resistivities (R,ohm-cm^{-1}) versus T (°K) plot within ± 0.5 log units of the line log R= 2.20 + 4000/T (for 298°-1573°K) were found to exhibit near-Nernstian response as pH sensors at low T or exhibit good Nernstian response at high T.

ZrO_2 pH electrodes exhibit chemical inertness, low drift rates, and lack of response to fO_2 or fH_2 at temperatures less than 573°K. Therefore, they are viable in studies of hydrothermal ore solutions, geothermal brines, and nuclear waste repository rock-water interactions. At T>873°K most Y_2O_3 - ZrO_2 cells begin to respond to the fO_2 of the environment; at 298 °K they have been found by Niedrach and us to withstand 0.6 kb pressure differentials. Thus, ZrO_2 pH sensors may even be extended beyond 573°K and 0.3 kb, but TEFLON or NAFION Eh sensors being developed are limited to this P and T.

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- ☐ 5 environmental geology
- ☐ 6 extraterrestrial geology
- ☐ 7 general geology
- ☒ 8 geochemistry
- ☐ 9 geology education
- ☐ 10 geomorphology
- ☐ 11 geophysics
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- ☐ 13 history of geology
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- ☐ 21 petrology, igneous
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- ☐ 23 petrology, sedimentary
- ☐ 24 Precambrian geology
- ☐ 25 Quaternary geology
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- ☐ 28 structural geology
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- ☐ 30 volcanology
- ☐ 31 other—describe below

_____

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Title of symposium for which your abstract was invited:

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⑤ OF THE AUTHORS ON THIS PAPER, HOW MANY ARE:

GSA Mbr/Fellow	5	Other Professional	_____
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⑥ SPEAKER'S IDENTITY AND CONTACT ADDRESS:
Speaker's name: Gene C. Ulmer
Address: Dept. of Geology, Temple University
City: Philadelphia State: PA Zip: 19122
Office Telephone: (Area Code) (215) 787-7171
Home Telephone: (Area Code) (215) 343-3689

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1/1/82

QUANTITATIVE MEASUREMENT OF HYDROTHERMAL REACTION PRODUCTS IN THE SYSTEM WASTE GROUNDWATER (DE-AC06-77RL01030)
Progress Report 4-20-82 to 5-20-82

TASK I. Results: pH Sensor

Our optimism for the excellent pH response of the Coors Y_2O_3-ZrO_2 material continues. Attached are nine graphs (Figures 1-9) that give the millivolt vs pH results at 90°C from Penn State. Testing, using a Ross Glass Electrode, these data seemed for the Coors tubes to be without short term drift, once a "seasoning-in" period of about 24 hours was past. Of note is the linear behavior in each case with the slope, as noted on each graph, being a high percentage of Nernstian response; the eight tested individual cells range from 72% to 94% with seven of the eight being 86% or better. Hence any of these Coors cells could be employed as a pH sensor with a suitable blank correction procedure which is, of course, typically necessary even with regular glass electrodes. Fig. 9 shows the Low Iron Zircoa-Corning cell which is only 60% Nernstian; its blank correction would be 40% of the measurement. It is also interesting to note that the tested Coors Cells consisted of three of 1/4"OD and three of 3/8"OD, fabricated in two separate lots at two separate times by Coors. Thus Coors has been able to maintain a high success quotient for us as compared to the Zircoa-Corning cells tested by Niedrach and MacDonald in which one useful cell in twenty-five was a typical success quotient.

The attached Fig. 10 is the follow up on our concern with the possibility of a change in charge carrier ZrO_2 from its high temperature anion conductivity in Y_2O_3-(fO_2 sensor) to its low temperature H^+ sensitivity (pH_2 sensor) and its low temperature "blindness" to either changes in fO_2 or fH_2 (dissolved gases in solution). The classic method of determining that a conductivity mechanism change has occurred in a material is to plot its conductivity (or resistivity) vs 1/T and note whether there has been a break in slope. If such a slope change is discovered, it signifies the temperature at which the mechanism change over occurs. Hence in Fig. 10, we have taken the high temperature fO_2 sensor data and linearly extrapolated it (wildly?) down temperature into the resistivity data generated at Penn State at 90°C and at room temperature. The Penn State measurements were done in a highly convenient, but not classical method. They simply measured the resistivity path between two platinum wires: one wire was inside the ZrO_2 cell filled with 3 N KCl and one wire was a few inches from the cell in a

beaker full of 3 N KCl aqueous solution into which the ZrO_2 cell had been submerged. The resistivity of this normality KCl is so low that the measured resistivity of the cell is little changed (±0.1 log) units) by the geometry of exact placement of the wires and cell.

The extrapolation of the high temperature data in Fig. 10 is observed to pass very close to portions of the clusters of data at 90°C and 25°C. The critically interesting point is that upon inspection of Fig. 10 and its legend it becomes clear that those cells which show any Nernstian pH response are within 0.6 log units of this line. Furthermore, the data thus far available indicate that the closer to the line, the better (higher % Nernstian) is the pH response. Data off the line entirely are for materials with no pH response.

While we started this resistivity study to concentrate on charge carrier mechanisms, it has turned out that we may have gained insight into a quick way of evaluating cell pH behavior. The resolution of our resistivity measurements may not be high enough to study subtle charge carrier mechanism changes; according to a recent paper by Kleitz etal (1981)* "--- intergrain conductivity [in Y_2O_3-ZrO_2] exhibits a break near 500°C. [The break is only about 0.1 log units, however]. This indicates a change in the conductivity mechanism. This point also merits further investigation". While we agree that further work on mechanism is desirable, the resolution of our resistivity data is sufficient to screen "good", "bad", and "no response" in terms of pH sensing. Thus, rather than begin a new direction of high resolution resistivity measurements at this time, the Penn State work will focus on the influence of grain boundary phases and density on the resistivity and pH response behavior of the Y_2O_3-ZrO_2 cells.

Attached is an abstract draft for our intended presentation at the national GSA in October 1982 in New Orleans.

TEST CHAMBER

The extension of the Coors pH sensor study to P > 1 bar T > 90°C has awaited the availability of a reaction vessel within our four Peter Gordon autoclaves. Since the Task 2 and 3 schedule has the autoclaves committed for months yet, we have built our own 50cc titanium-lined vessel for P ≦ 300 atm and T ≦ 300°C. As you know, a solution pump and gating valves are on order with delivery promised within 3 weeks. The reaction vessel is machined; the furnace is being built. The closure gland to hold the Coors tubes in the vessel are being researched for us Mr. A. Salter of the Conax Corp. The need to have a 'non-spitting' gland has also been addressed by Niedrach at G.E. Corp.

*P.318 Kleitz, M., Bernard, H., Fernandez, E., and Schouler, E. (1981) Impedance spectroscopy and electrical resistance measurements on stabilized zirconia. in Advances in Ceramics, vol.3, edited by Heuer and Hobbs, Amer. Cer. Soc.

For intermediate testing (200 bars-200°C) PTE (Teflon) may be adequate but for the eventual interest in higher P+T (300 bars-300°C) a boron nitrite sealant is being tried for us by Salter. Hence by June we hope to be collecting pH sensor data at P+T conditions closer to the desired goals of this project.

NAFION SENSOR

After months of waiting, General Electric has supplied us with a complimentary prefabricated Nafion sensor membrane with platinized electrodes already attached. A housing suitable for our testing must be machined for this membrane. Our test will be to see if the NAFION system remains Nernstian as an fH_2 (gaseous) sensor upto 200 to 250°C as no data exist beyond 160°C.

TASKS II and III.

A topical report, "Hydrothermal reaction of Columbia River basalt and Hanford groundwater" and a preliminary report "Initial results of hydrothermal reaction in the system spent fuel/groundwater/basalt at 300°C and 300 bars were submitted to Rockwell.

The gold tubes required to line the sampling stems were received and are being installed. The second Dickson rocking autoclave should be operational within the next month.

Two experiments are in progress or preparation:
(1). Basalt/water: 300°C, 300 bars, water:rock mass ratio 20:1. This experiment will complete a series in which the mass ratio has been varied. Ratios studied were 5, 10, and 20. The experiment at a mass ratio of 10 should be repeated. That experiment utilized the original Grande Ronde composition, whereas subsequent experiments have used the revised composition. In order to reduce the number of variables to a minimum, this 10 mass ratio experiment should be repeated using the revised solution composition. This should allow identification of the mechanism by which initial pH depression is produced.

(2). Basalt/spent fuel/water: 200°C, 300 bars, water:spent fuel:basalt mass ratio 20:1:1.

As soon as the new rocking autoclave has been tested we intend to proceed with additional experiments. Among the experiments which we propose are:
(1). Basalt/water: 300°C, 300 bars, water:rock mass ratio 10:1, short duration. This experiment would use a finer grain-size basalt fraction to determine possible effects of grain size.

(2) Basalt/water: 300°C, 300 bars, water:rock mass ratio 10:1, short duration. This proposed experiment would utilize basalt which is not cleaned using the HF treatment. This would allow us to identify possible effects of the HF surface cleaning procedure.

(3). Basalt/water: 150°C, 300 bars, water:rock mass ratio 10:1. Long duration experiment investigating lower temperatures.

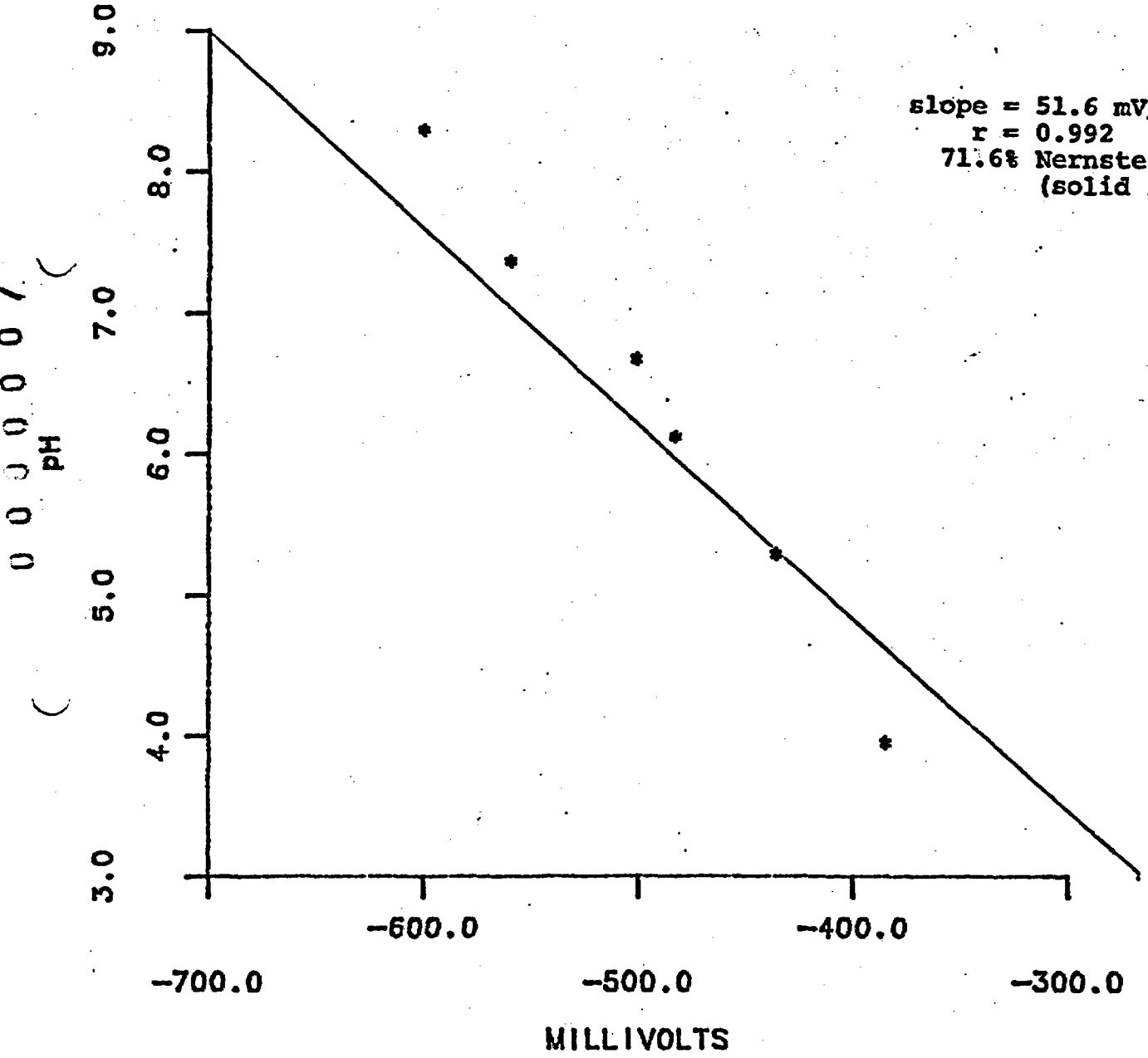
(4). Spent fuel/water: 300°C, 300 bars, water:spent fuel mass 10:1. To determine reaction of spent fuel alone.

We also propose a number of spent fuel/basalt/water experiments in which the basalt/spent fuel mass/ratio is varied. Exact mass ratios to be investigated should be discussed. Indeed, the matrix of experimental parameters to be investigated should be thoroughly discussed within the next month.

4/9/82

Tests of Coors Tubes at 90°C

VERSUS Commercial (Ross) Glass Electrode



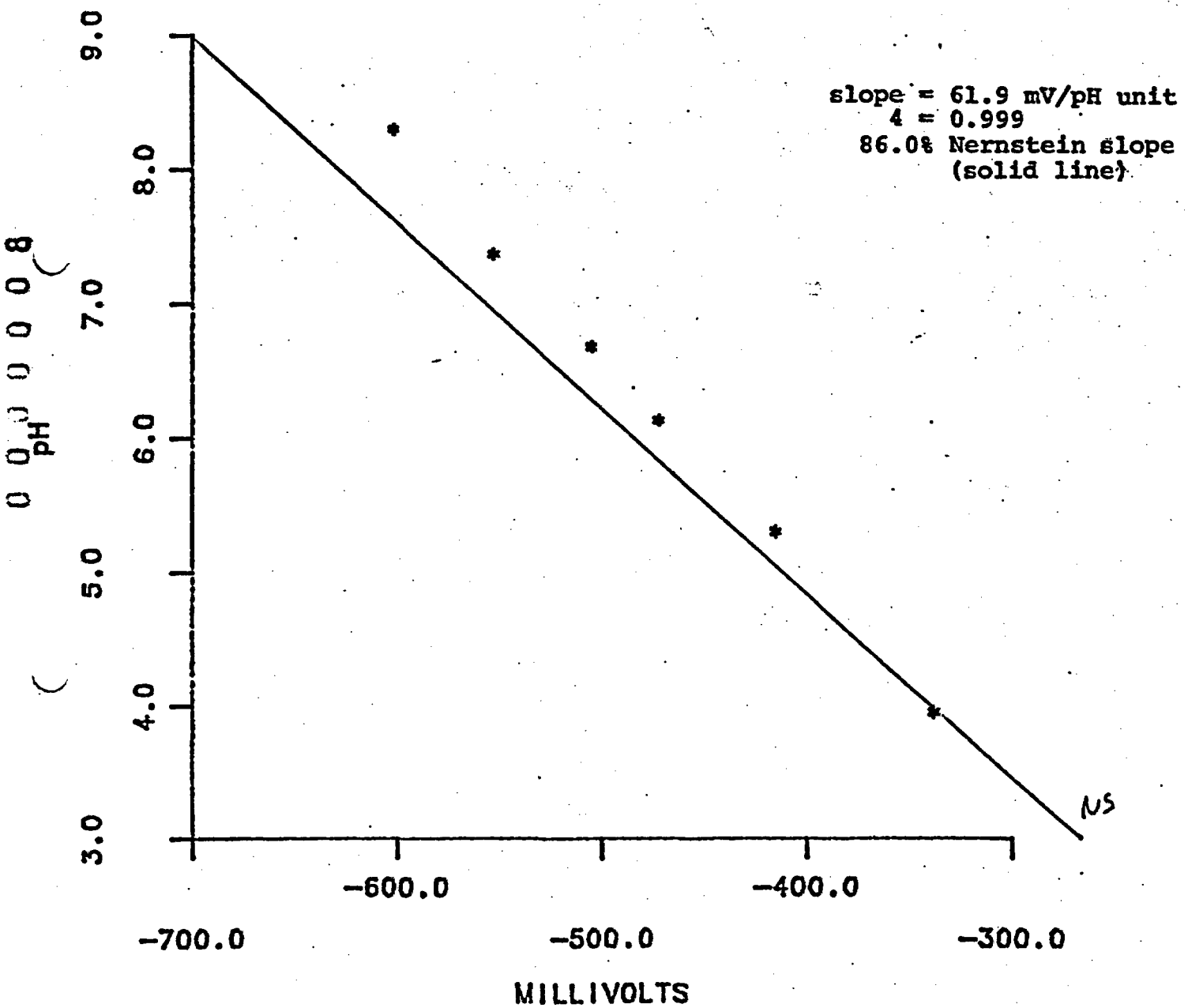
Tube CT-1-3/8

Fig. 1

4/9/82

Tests of Coors Tubes at 90°C

VERSUS Commercial (Ross) Glass Electrode



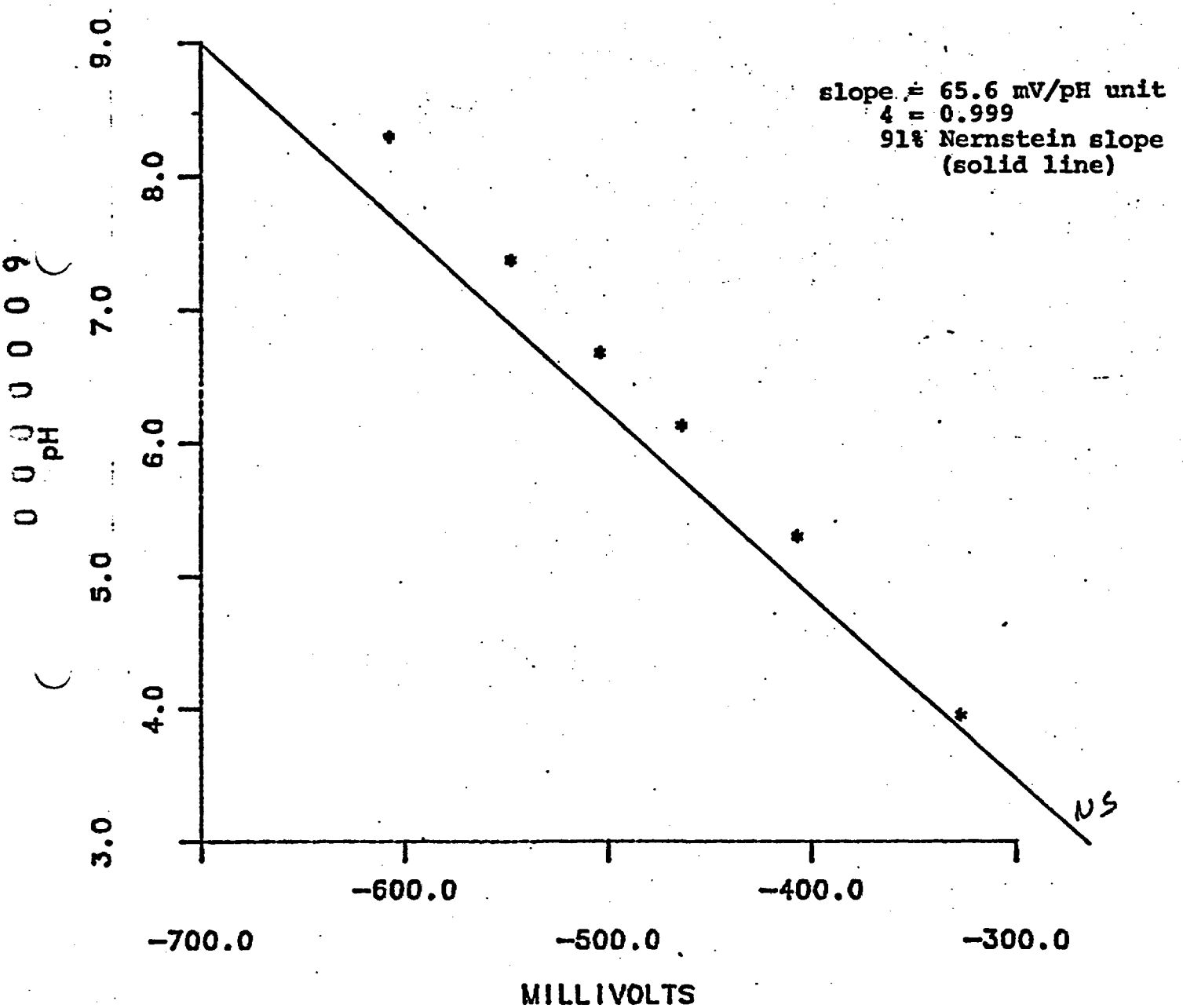
Tube CT-3-3/8

Fig. 2

4/9/82

Tests of Coors Tubes at 90°C

VERSUS Commercial (Ross) Glass Electrode



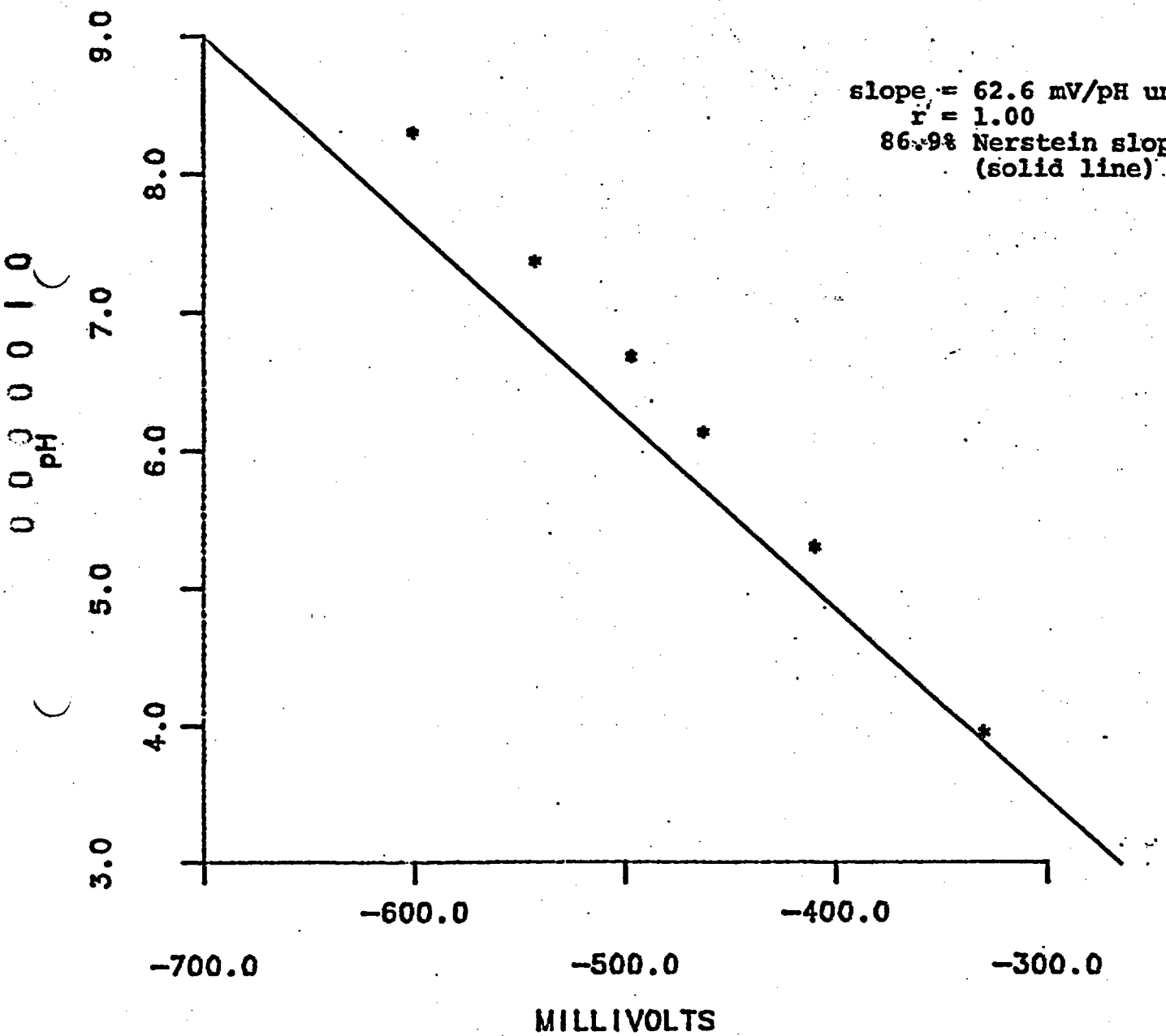
Tube CT-1-1/4

Fig. 3

4/9/82

Tests of Coors Tubes at 90°C

VERSUS Commercial (Ross) Glass Electrode



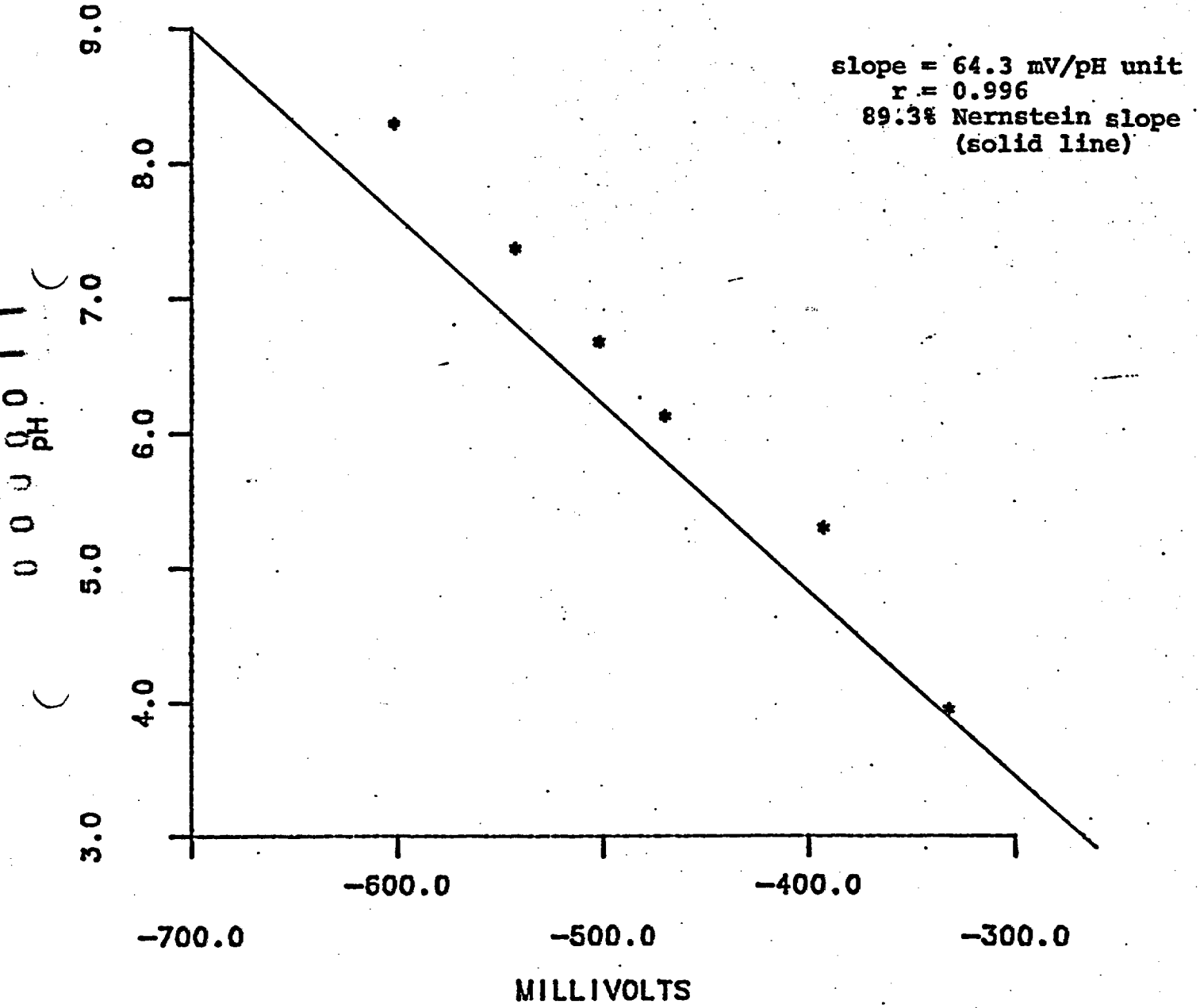
Tube CT-2-1/4

Fig. 4

4/9/82

Tests of Coors Tubes at 90°C

VERSUS Commercial (Ross) Glass Electrode

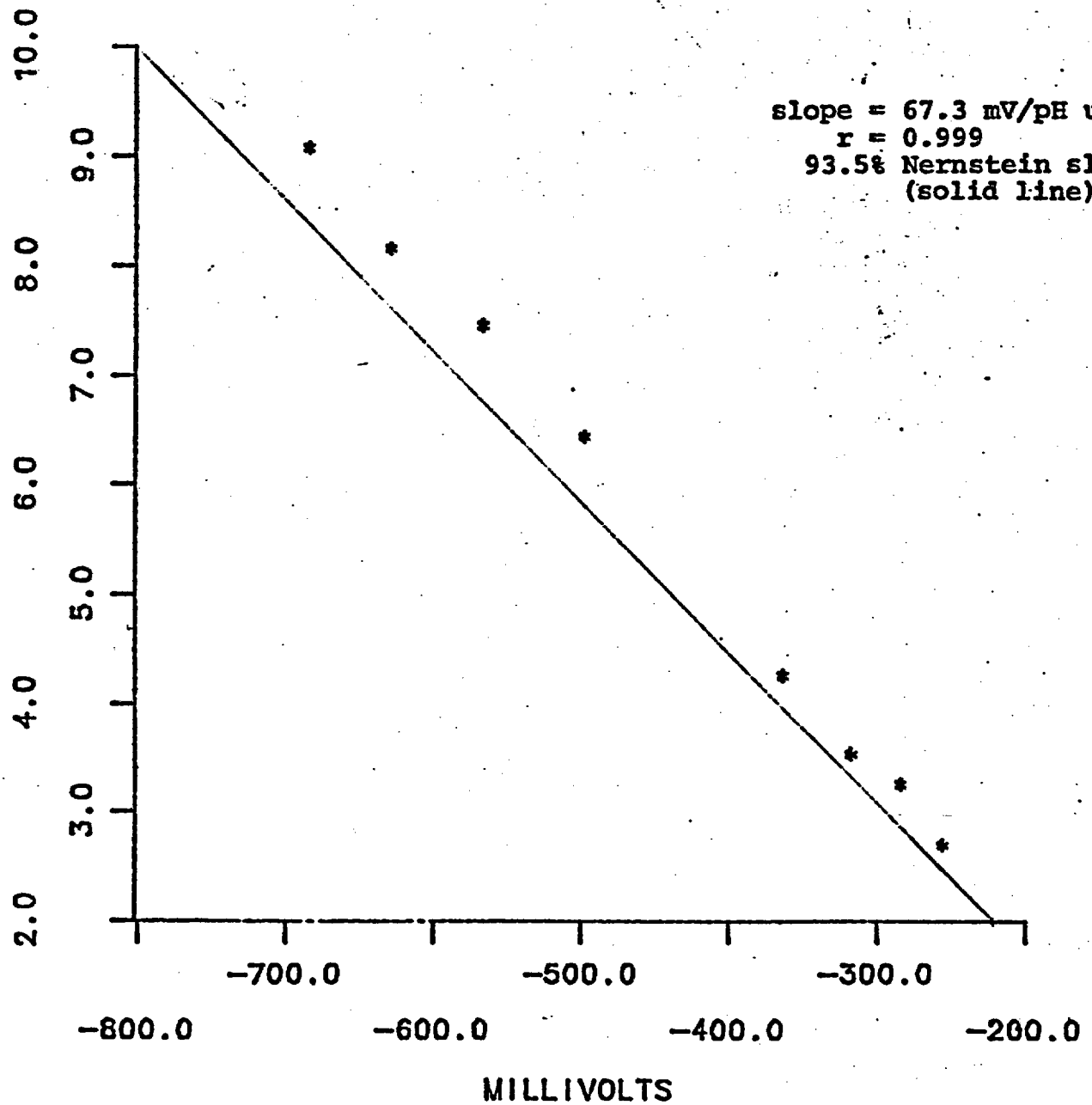


Tube CT-3-1/4

Fig. 5

Tests of Coors Tubes at 90°C

VERSUS Commercial (Ross) Glass Electrode



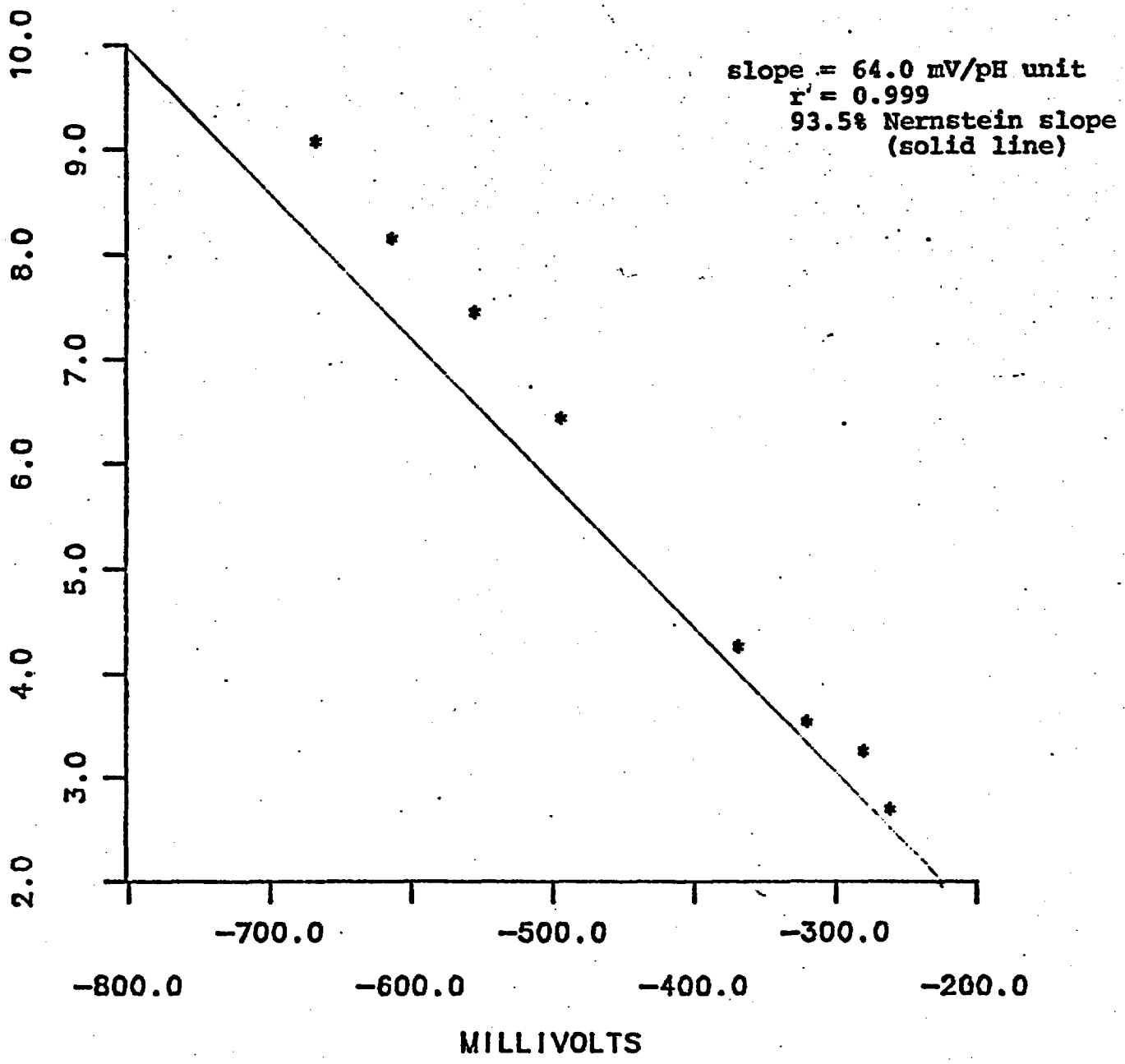
Tube CT-4-3/8

Fig. 6

4/10/82

Tests of Coors Tubes at 90°C

VERSUS Commercial (Ross) Glass Electrode



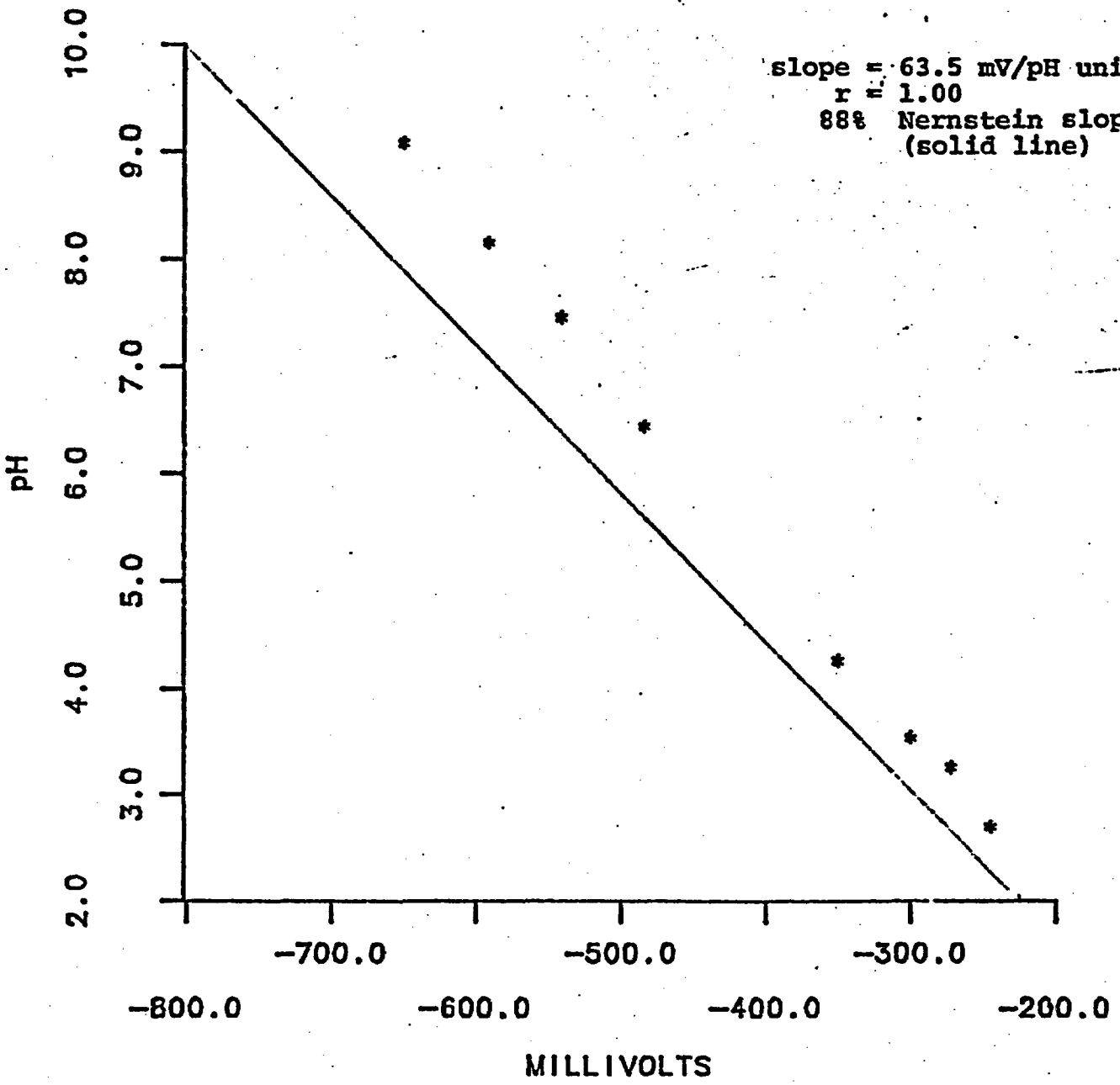
Tube CT-2-3/8

Fig. 7

4/10/82

Tests of Coors Tubes at 90°C

VERSUS Commercial (Ross) Glass Electrode



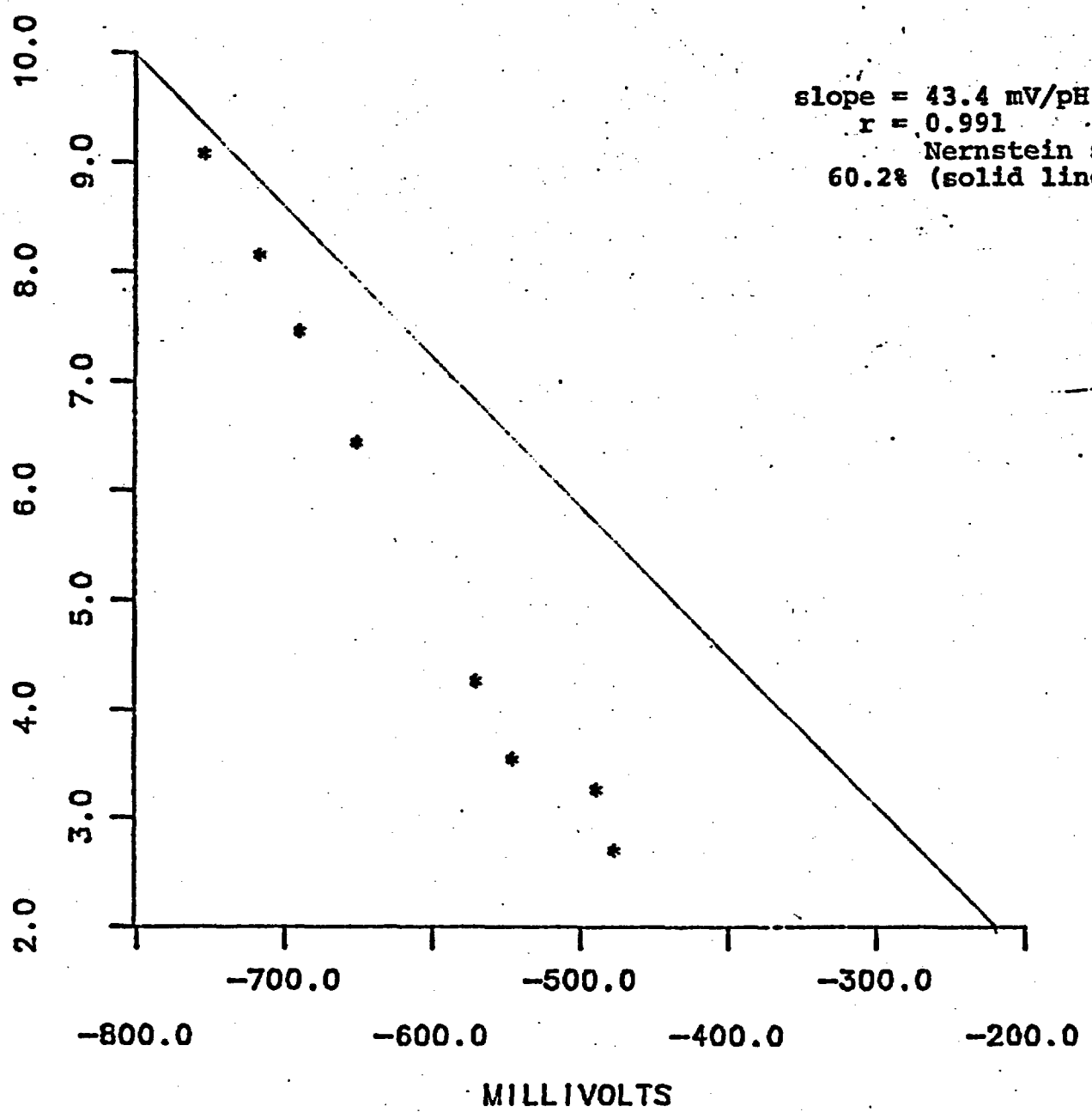
Tube CT-1-1/4

Fig. 8

4/10/82

Tests of Zircoa Tube at 90°C

VERSUS Commercial (Ross) Glass Electrode



Tube ZT-L1-1

Fig. 9

Log Resistivity vs Reciprocal Temperature
for Y_2O_3-ZrO_2 Materials

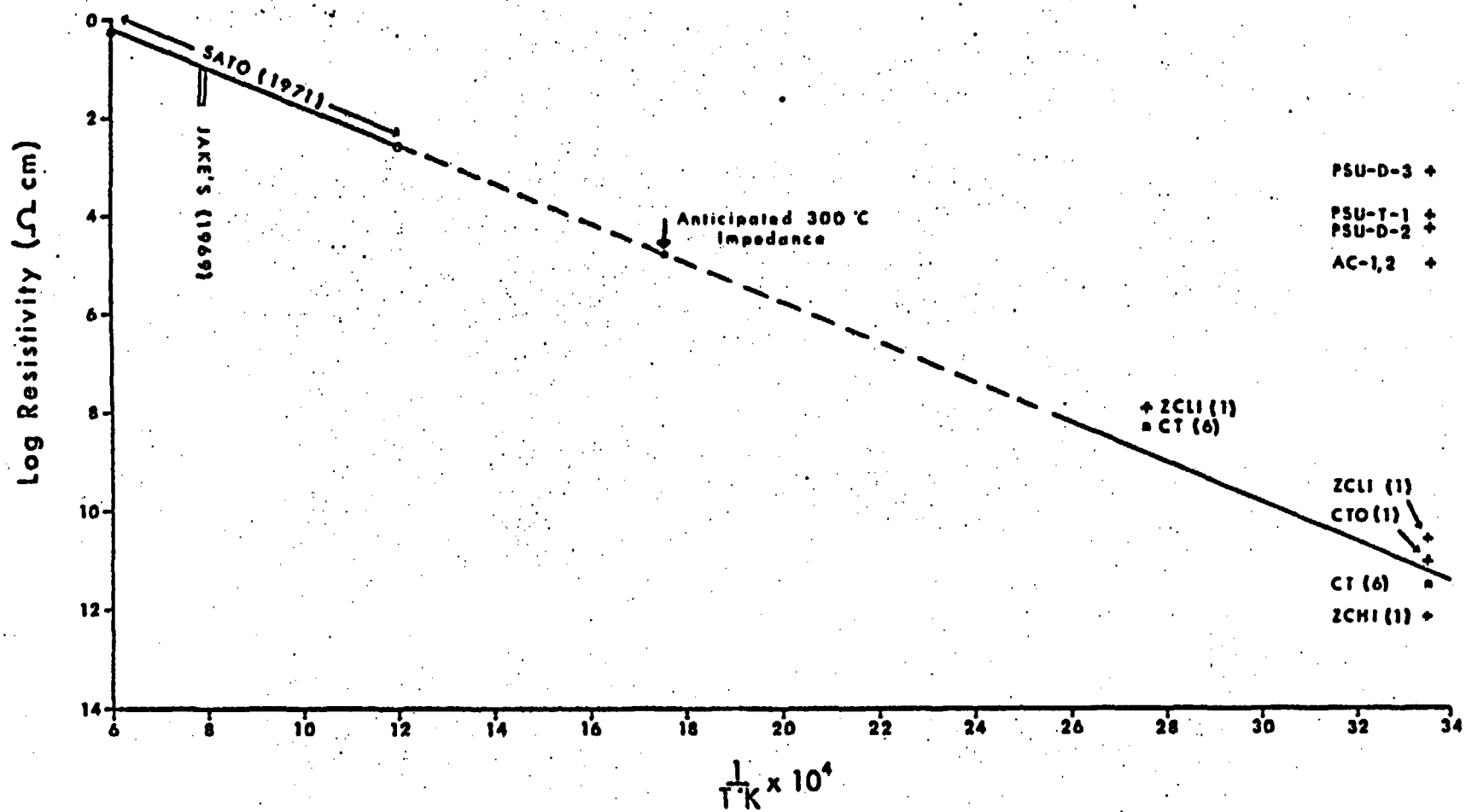


Fig. 10

Caption to Figure 10 - Log Resistivity vs Reciprocal Temperature for Y_2O_3 - ZrO_2 Materials

Hi Temperature Data for 9 mole % Y_2O_3 - ZrO_2 Materials

- Review by Sato of literature available in 1971

  Sato, M. (1971) Solid Electrolyte Fugacity Sensors in Research Technique for High Pressure and High Temperature, edited by G.C. Ulmer.

- Jakes review of the influence of % anion vacancy in Y_2O_3 - ZrO_2 on its resistivity over the range of 2-8% (latter % is lowest resistivity)

  Jakes, D. (1969) Galvanicke clankys pernymi electrolyty. Chem. Listy, 63 : 1073 - 1091.

- Anticipated 300°C behavior by linear extrapolation of high temperature data.

PSU lower temperature data: N = Nernstian, NR = No Response

+	ZCLI	One cell of Zircoa Corning Low Iron - 60% N	
	CT	Average for six cells of Coors materials	90% N
+	PSU-D-3	Ceramic Dept. PSU, Disk #3	NR
+	PSU-T-1	Ibid, Tube #1	NR
+	PSU-D-2	Ibid, Disk #2	NR
+	AC-1,2	Australian Cells #1140 and #1378	NR
+	CTO	Original Coors Tube	90% N
+	ZCHI-	One sample of Zircoa Corning Standard (which is high iron)	NR

Monthly and Cumulate Costs Incurred and Anticipated Expenditures for FY 82.

Budget Categories	Budgeted Costs	Monthly Expenses	Cumulate 10/1/80-5/31/82	June	Anticipated July	August	September	Total	Remaining
Salaries, Wages Fringe Bene.	81,277.	5,406.	43,251.	9,835.	13,175.	8,848.	5,574.	80,683.	594.
Supplies and Operating Exp.	9,712.*	2,639.	12,322	300.	300.	300.	300.	13,522.	(3810.)*
Travel	5,840.	200.	5,513	0.	0.	0.	250.	5,763.	77.
Penn State Subcontract	31,721.	2,644.	21,150.	2,644.	2,644.	2,644.	2,644.	317,721.	0.
Computer and Equipment	6,150.	140.	335.	700.	1,000.	2,600.	530.	4,665.	1,485.
Total Direct	134,700	11,029.	82,571.	13,479.	17,119.	14,392.	9,298.	136,859.	(2,159.)*
Indirect	40,300.	2,123.	20,576.	6,285.	5,645.	4,581.	2,500.	39,687	613.
Total	175,000.	12,215.	103,147.	19,764.	22,764.	18,973.	11,898.	176,546.	(1,546.)*

*These totals are not corrected to reflect $1,950. additional funds provided by Rockwell to cover purchase of high-pressure pumps and accessories.

TEMPLE UNIVERSITY
OF THE COMMONWEALTH SYSTEM OF HIGHER EDUCATION
PHILADELPHIA, PENNSYLVANIA 19122

DEPARTMENT OF GEOLOGY
D. E. Grandstaff

May 20, 1982

0 0 0 0 0 4 9

Darlene Schatz
Rockwell Hanford Operations
Energy Systems Group
P. O. Box 800
Richland, WA 99352

Dear Darlene,

We have recently received the shipments of gold tubes and thimbles. The received weights are as follows:

exit tube gold liners	#1.	28.80 g
	#2.	28.78 g
gold thimbles	#1.	131.14 g
	#2.	126.95 g

Total weight of the new gold shipment, according to our measurements, was 315.67 g.

Weight of gold previously shipped to us by Rockwell (received 2/15/81) was 347.23 g, according to our records. Thus the total inventory of gold in our possession is 662.9 g. Most of the old shipment of gold cannot be reweighed at this time to determine present weight as it is in use in the Dickson autoclaves. We anticipate that a small amount of gold may have been lost, particularly in production of gold shavings for use in the gold filter. The amount of gold lost in this process is probably less than 1 g.

If you have any questions concerning the gold inventory, please contact me.

Sincerely,

David

David E. Grandstaff